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NRCC/IMRI SYMPOSIUM SERIES
"POLYBLENDS-'87", APRIL 28 and 29, 1987

Co-Chairmen: B.D. Favis and L.A. Utracki

FINAL PROGRAM

April 28th, 1987

- 08:00 REGISTRATION
- 08:30 INTRODUCTION
- 08:35 1. J.W. BARLOW and D.R. PAUL, "THE IMPORTANCE OF ENTHALPIC INTERACTIONS IN POLYMERIC SYSTEMS", University of Texas at Austin, Austin, Texas.
- 09:35 2. R.W. HOHLFELD, "OXAZOLINE REACTIVE POLYMERS", Dow Chemical U.S.A., Midland, Michigan.
- 10:00 PAUSE
- 10:30 G.L. BATA: "WELCOMING REMARKS"
- 10:45 3. *ROBERT E. PRUD'HOMME and GARY FAIRLEY, "POLYETHYLENE/NYLON BLENDS", Laval University, Québec, Canada.
- 11:15 4. A. NATANSOHN, M. RUTKOWSKA and A. EISENBERG, "NMR STUDIES OF IONOMERS 6. POLYURETHANE - POLYPHOSPHONATE BLENDS", McGill University, Montreal, Canada.
- 11:45 5. *K.S. SHIH and C.L. BEATTY, "EFFECT OF MOLECULAR WEIGHT ON THE COMPATIBILITY OF POLYCARBONATE AND POLY(HEXAMETHYLENE SEBACATE) BLENDS", University of Florida, Gainesville, Florida.
- 12:30 LUNCH

- 14:00 6.* C.C. HSU and P.H. GEIL, "STRUCTURE-PROPERTY-PROCESSING RELATIONSHIPS OF POLYPROPYLENE-POLYBUTYLENE BLENDS", University of Illinois, Urbana, Illinois.
- 14:30 7. D.R. WIFF¹, W-F. HWANG², HOE H. CHUAH³ and E.J. SOLASKI³, "THERMAL ANALYSIS STUDIES ON THERMOPLASTIC RIGID ROD MOLECULAR COMPOSITES",
¹GenCorp, Akron, Ohio; ²Dow Chemical, Midland, Michigan;
³University of Dayton, Dayton, Ohio.
- 15:00 PAUSE
- 15:30 8. E.C. KELUSKY, C.T. ELSTON and R.E. MURRAY, "CHARACTERIZING POLYETHYLENE BASED BLENDS WITH TEMPERATURE RISING ELUTION FRACTIONATION (TREF) TECHNIQUES", Du Pont Canada Inc., Kingston, Ontario.
- 16:00 9. P.M. SUBRAMANIAN, "POLYETHYLENE TEREPHTHALATE BLENDS FOR PERMEABILITY BARRIER APPLICATIONS", Du Pont, Wilmington, DE, USA.
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April 29th, 1987

- 08:30 10. L.A. UTRACKI, "PRESENT AND FUTURE TRENDS IN ENGINEERING POLYMER BLENDS TECHNOLOGY", National Research Council of Canada, Industrial Materials Research Institute, Boucherville, Quebec.
- 09:30 11. D.V. HOWE and D. WOLKOWICZ, "STRUCTURE PROPERTY RELATIONS IN POLYAMIDE-ABS BLENDS", Borg-Warner Chemicals, WV, U.S.A.
- 10:00 PAUSE
- 10:30 12. B.D. FAVIS and J.P. CHALIFOUX, "THE EFFECT OF VISCOSITY RATIO ON THE MORPHOLOGY OF POLYPROPYLENE/POLYCARBONATE BLENDS DURING PROCESSING", National Research Council of Canada, Industrial Materials Research Institute, Boucherville, Quebec.

- 11:00 13. P. CIELO, B.D. FAVIS and X. MALDAGUE, "LIGHT-SCATTERING CHARACTERIZATION OF POLYBLENDS IN THE PRESENCE OF MULTIPLE-SCATTERING CONDITIONS", National Research Council of Canada, Industrial Materials Research Institute, Boucherville, Quebec.
- 11:30 14. T.F. BLAHOVICI and G.R. BROWN, "OXYGEN PERMEATION OF BLENDS OF COPOLYMERS OF SILOXANES AND POLY(METHYLMETHACRYLATE)", McGill University, Montreal, Quebec.
- 12:30 LUNCH
- 14:00 15. A. GARTON, W.T. STEVENSON, J.N. CLARK, J.H. DALY and P.D. McLEAN, "ADDITIVES TO IMPROVE THE STRENGTH, STIFFNESS AND TOUGHNESS OF EPOXY RESINS", National Research Council of Canada, Division of Chemistry, Ottawa, Ontario.
- 14:30 16. M.M. DUMOULIN, L.A. UTRACKI* and P.J. CARREAU, "RHEOLOGICAL PROPERTIES OF LLDPE/PP BLENDS, PART 2: SOLID STATE BEHAVIOR", Ecole Polytechnique, Montreal, Quebec; *National Research Council of Canada, Industrial Materials Research Institute, Boucherville, Quebec.
- 15:00 PAUSE
- 15:30 17. W.E. BAKER and M. SALEEM, "POLYSTYRENE-POLYETHYLENE MELT BLENDS OBTAINED THROUGH REACTIVE MIXING PROCESS", Queen's University, Kingston, Ontario.
- 16:00 18. A. GOLOVOY, M.-F. CHEUNG and H. VAN OENE, "THE PHASE BEHAVIOR AND MECHANICAL PROPERTIES OF POLYARYLATE AND POLYCARBONATE BLENDS", Ford Motor Company, Dearborn, Michigan.

* Manuscript not received on time. Please communicate directly with the author.

INTRODUCTION

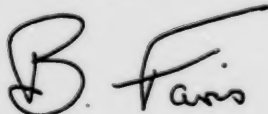
Polymer blends by definition are physical mixtures of different homo or copolymers. There are several sound economic advantages to blending, it can: 1) generate a unique material as far as properties and/or processability are concerned; 2) extend the performance of expensive resins; 3) allow for the quick modification of performance; 4) extend plant capacity since most polymer blends are processed on standard processing equipment; 5) be achieved through low capital investment; 6) be accomplished much more rapidly than developing a totally new polymer and 7) allow recycling of scrap.

In the USA in 1985 polymer blends and alloys accounted for 20% of the synthetic resin market. The sales of engineering blends based on polyphenyleneether amounts to about one billion dollars a year. Blends with engineering resins have been the center of significant R & D activity. Commercial utilization of engineering blends has been predicted to grow at $\approx 17\%$ /year and represents the most active growth area in polymer blends as a whole.

From the thermodynamic standpoint the great majority of polymers are immiscible and most "blends of commerce" belong to this type. Significant emphasis continues to be placed on methods of improving the interfacial adhesion between the matrix and the dispersed phase. Another area of importance is an understanding of structure development during processing. Immiscible blends have a deformable minor phase and under the appropriate conditions morphological structures such as spheres, ellipsoids, fibres and plates/ribbons can be generated. Control of these can be very complex. In the program of "Polyblends-'87" blends with engineering resins are emphasized. In particular the importance of interfacial modification and morphology are considered.

"Polyblends-'87" is the 8th symposium in the series on polymer alloys and blends, organized and sponsored by the Industrial Materials Research Institute of the National Research Council of Canada. The previous seven have been published in Polymer Engineering and Science: 22 (2), 22 (17), 24 (2), 24 (17), 26 (1), 27 (5) and 27 (6). The two other symposia series are on modeling of plastics processing and on composites, published respectively in Polymer Engineering and Science and in Polymer Composites. Proceedings of these meetings are recorded and the tapes of the presentations and discussions are kept in the NRCC/IMRI library for a period of two years, available to anyone interested in the subject.

As organizers of this symposium we take great pleasure in welcoming you.



B.D. Favis and L.A. Utracki

THE IMPORTANCE OF ENTHALPIC INTERACTIONS IN POLYMERIC SYSTEMS

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ABSTRACT

Enthalpic interactions between blend components primarily determine the state of miscibility and many of the physical properties of the blend. Recent applications of these thermodynamic considerations are reviewed for a variety of systems, including binary and ternary blends of homopolymers, binary blends of copolymers with homopolymers, and polymer-solvent mixtures. Recent advances toward predicting polymer blend miscibility through use of a modified quasichemical thermodynamic model and heats of mixing data for low molecular weight liquids are also discussed.

Presented at the NRCC-IMRI symposium "Polyblends-'87"

Boucherville, Quebec, April 28 and 29, 1987

INTRODUCTION

This review briefly explores several recent developments which emphasize the importance of enthalpic interactions to the behavior of polymer systems. While generally focused on the importance of polymer-polymer interactions to understanding the phase behavior and mechanical properties of both miscible and immiscible polymer blends, this review has been broadened to also consider recent work toward a priori prediction of polymer blend miscibility with modern thermodynamic, group contribution, theories and development of a predictive theory for describing enthalpically driven sorption of solvent vapors in polymers. Given the broad range of topics considered, this review is necessarily limited in the detail provided in each area. Despite this limitation, the authors hope that it will inspire other researchers to carefully consider the use of enthalpic interactions for solving a variety of practical problems in polymeric systems.

PHASE BEHAVIOR OF MULTICOMPONENT POLYMER BLENDS

The importance of enthalpic interactions to the phase behavior of polymer blend systems has long been recognized. For example, the formation of miscible binary blends depends primarily on the presence of enthalpic interactions between the blend components which give rise to exothermic heats of mixing. This assertion follows directly from consideration of the relative contributions of the heat of mixing, ΔH_{mix} , and the entropy of mixing, ΔS_{mix} , to the free energy of mixing, ΔG_{mix} ,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1)$$

Miscibility requires that ΔG_{mix} be negative and satisfy the additional requirement that $\partial^2 \Delta G_{mix} / \partial \phi_1^2 > 0$ to ensure stability against phase segregation. Since ΔS_{mix} is always positive, ΔG_{mix} can be negative even when ΔH_{mix} is small and positive, as is the

case for many solutions of small molecules. For mixtures of polymeric molecules, however, zero order approximations for ΔS_{mix} , such as that by Flory and Huggins (1-3), clearly show that this term is too small to drive ΔG_{mix} negative when the component molecular weights are greater than a few thousand, unless ΔH_{mix} is a very small positive number. The Flory-Huggins treatment assumes that the heat of mixing follows a van Laar relationship with blend composition,

$$\Delta H_{\text{mix}} = (V_A + V_B) B \phi_A \phi_B \quad (2)$$

where V_1 is the volume of component 1 in the blend and ϕ_1 is its volume fraction in the binary mixture. The parameter B in equation (2) is an interaction energy for mixing segments of the two components and can alternately be expressed as a chi parameter (1), via,

$$B/RT = x_A/v_A = x_B/v_B = x_{AB} \quad (3)$$

where v_1 is the segmental molar volume, as often seen in the polymer literature. Two important conclusions can be reached from equations (1)-(3). First of all, the B or χ parameter must be negative, implying an exothermic heat of mixing, if a miscible blend is to form spontaneously on mixing of high molecular weight polymers A and B. Secondly, the B parameter is independent of molecular weights of the blend components. This second conclusion permits the use of analog calorimetry to predict polymer-polymer miscibility, as discussed in following sections.

Heats of mixing cannot be measured directly for the polymer mixture, however thermodynamic analyses of miscible blend properties such as the melting point depression shown by crystallizable blend components (4-8), the reduction of solvent sorption (9-13), the presence in many miscible blends of Lower Critical Solution Temperature, LCST, behavior (14-16), various spectroscopic measurements (17-23), and scattering techniques (24-27), all suggest the presence of exothermic heats of mixing

between blend components. Several of these techniques provide a basis for quantitatively assessing the magnitude of the interaction parameter B.

An example of the consistency with which B can be obtained by different experimental methods is illustrated in Figure 1 for Phenoxy/polyester blends and their analogs (12,28). Here it is seen that B values obtained from the melting point depressions of various crystallizable polyesters in Phenoxy agree fairly well with B values obtained by measuring the reduced sorption of methylene dichloride vapor in the polymer blend melt. These measurements are, in turn, consistent with B values obtained from measurements of ΔH_{mix} for low molecular weight esters with diphenoxypropanol, a reasonable analog for the Phenoxy repeat structure.

Figure 1 also suggests that a range of polyester compositions exists for miscibility with Phenoxy. The polyesters and esters are imagined to consist of two types of units; ester carbonyl and aliphatic, CH_2 or CH_3 , moieties, and the repeat unit composition is expressed as the volume fraction of the aliphatic species. The B parameters are positive and the blends immiscible for volume fractions of aliphatic carbon in the repeat unit less than 0.7 or greater than 0.87. Between these limits the blends are miscible, and B is negative and follows a roughly parabolic variation with polyester or ester composition with a maximum negative value near 0.8 volume fraction aliphatic carbon. Similar variations of B with blend component structure have been observed in a variety of binary blend systems, and the phenomenon is apparently quite general (28-35). Attempts to explain the variation of B with component structure have led to the multicomponent thermodynamic models discussed below.

Binary Interaction Models Several investigators (36-40) have proposed models for describing ΔH_{mix} in terms of a series of binary interactions between the various species involved. In its simplest form (1,36) this amounts to writing

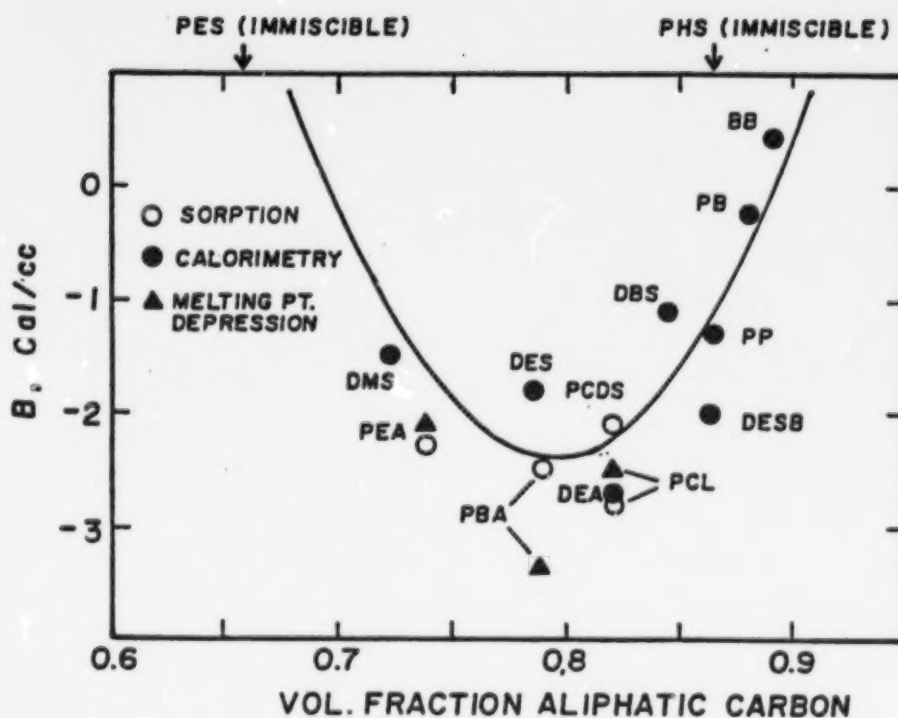


Figure 1. Variation of Interaction Parameter with Polyester Composition for Polyester/Phenoxy Blends (28).

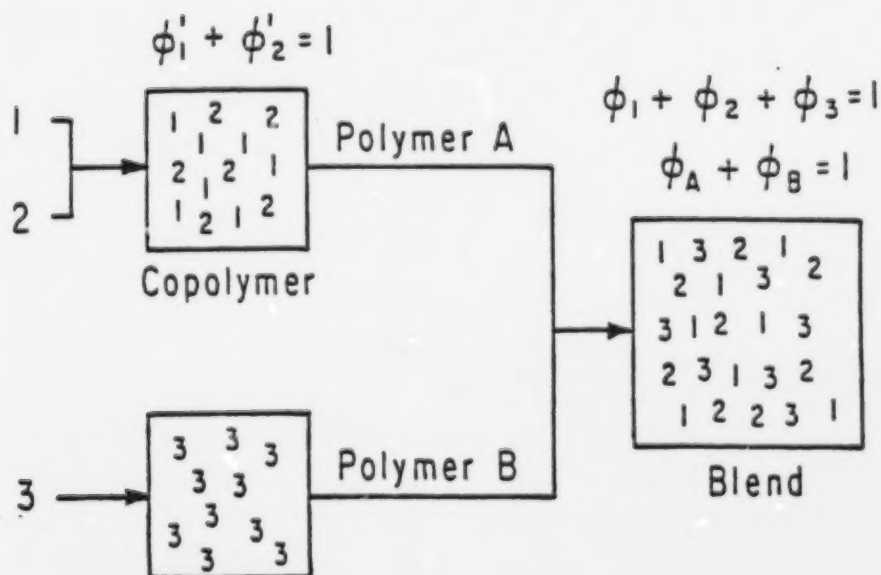


Figure 2. Schematic for Calculating the Heat of Mixing of a Copolymer with a Homopolymer (36).

$$\Delta H_{\text{mix}}/V = \sum_i \sum_{j \neq i} B_{ij} \phi_j \phi_i \quad (4)$$

where ϕ_i is the volume fraction of species i in the multicomponent mixture and B_{ij} is the binary interaction between species i and species j . Provided one identifies B_{ij} with the interaction between polymer repeat unit i and polymer repeat unit j , equation (4) can be used directly to describe miscibility of multicomponent polymer blends, as discussed below.

By redefining i and j to mean structural units within the repeat units of the polymer components, equation (4) can also be applied to the variation of ΔH_{mix} with polymer component structure seen in Figure 1. For this purpose, it is conceptually convenient to divide the repeat units of each component polymer into the desired structural units, see Figure 2, and to use equation (4) to calculate the heat of mixing of the structural units as if these units existed as pure components. This calculation does not directly give the heat of mixing of the blend components, however, because each repeat unit is now also a mixture of structural units, and the heats of mixing associated with forming the structural unit of each repeat unit must be subtracted from that of forming the mixture directly from the structural units. This procedure gives

$$\Delta H_{\text{mix}}/V = \sum_i \sum_{j \neq i} B_{ij} \phi_i \phi_j - \sum_k \psi_k \sum_i \sum_{j \neq i} B_{ij} \phi_1^k \phi_j^k \quad (5)$$

where ψ_k is the volume fraction of polymer k in the blend, ϕ_1^k is the volume fraction of structural unit i in polymer k , and where

$$\sum_k \psi_k \phi_1^k = \phi_i \quad (6)$$

$$\sum_k \psi_k = 1$$

describe the continuity of species i and system volume, respectively.

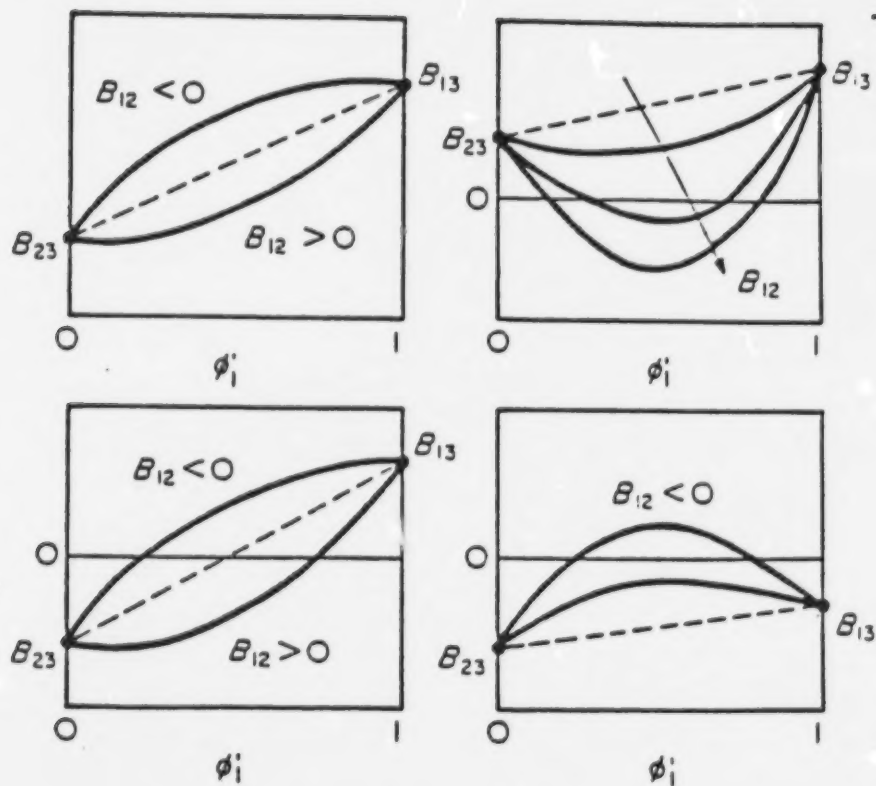


Figure 3. Illustrations of Ways the Interaction Parameter may Vary with Copolymer Composition (36).

Equation (5) suggests that miscible polymer blends, as characterized by $\Delta H_{\text{mix}} < 0$, are possible even when all of the interaction parameters, B_{ij} , between their structural units are positive. This is most easily seen for the simple case, illustrated in Figure 2, of mixing a copolymer A with a homopolymer B. For this case, equation (5) can be easily rewritten to give

$$\Delta H_{\text{mix}} = B \psi_A \psi_B \quad (7)$$

where B is the interaction parameter for mixing A with B,

$$B = B_{13} \phi_1^A + B_{23} \phi_2^A - B_{12} \phi_1^A \phi_2^A \quad (8)$$

As illustrated in Figure 3, B and ΔH_{mix} vary parabolically with copolymer composition, and if B_{12} is a large enough positive value, that is (36) if $(B_{12})^{1/2} > (B_{13})^{1/2} + (B_{23})^{1/2}$, there will be a region in copolymer composition for which B and ΔH_{mix} are negative. This simple result would appear to explain the "miscibility window" with structural variation shown in Figure 1 and seen in many different systems. Physically, it occurs because the addition of polymer B to the copolymer dilutes the highly unfavorable interactions within the pure copolymer between structural units 1 and 2 (ester carbonyl and CH_x units in the polyesters of Figure 1).

Miscible Blends of Homopolymers with Copolymers The analysis above suggests that a whole class of miscible polymer blends may exist in which ΔH_{mix} is not negative because of the presence of specific, exothermic, interactions between blend components. That is not to say that such interactions do not exist nor that specific interactions do not provide the necessary enthalpic driving force for miscibility in some systems (20,41). It does suggest, however, that the possibilities for forming miscible blends may be far better than previously thought.

There are many examples in the literature where the

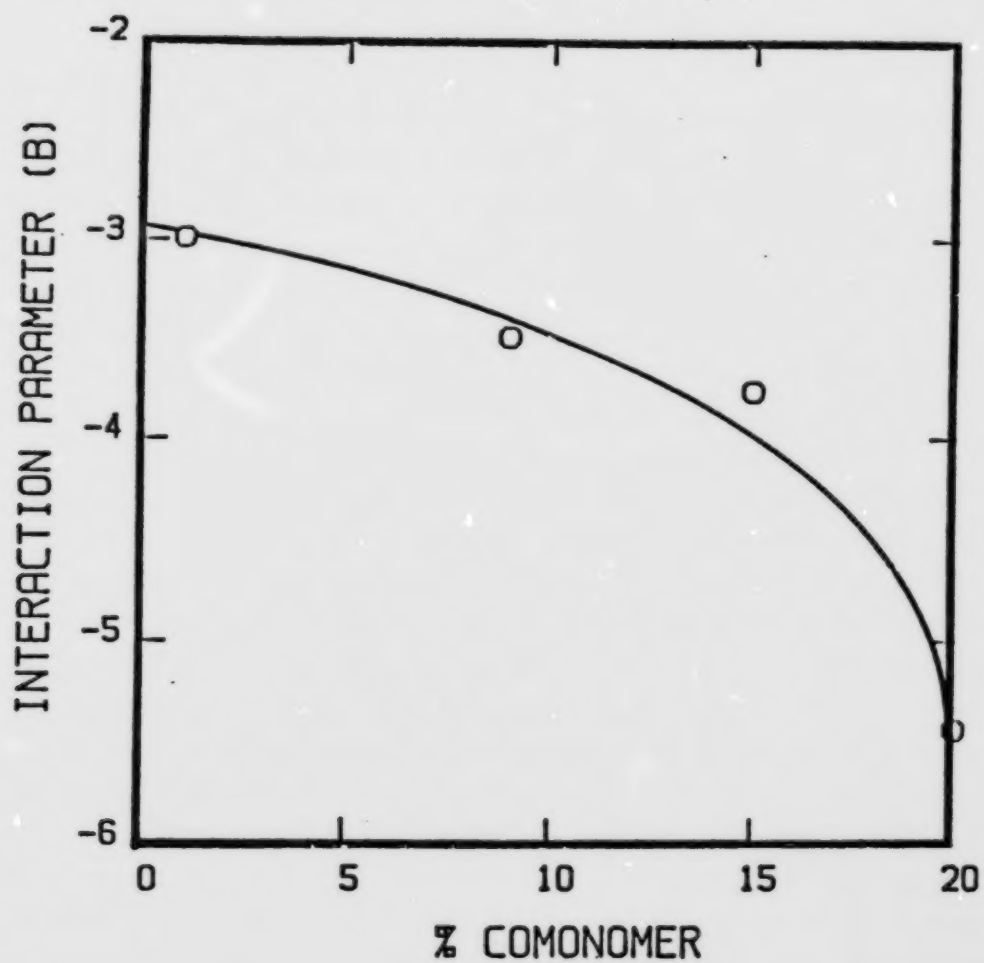


Figure 4. Variation of the Interaction Parameter with Copolymer Composition for Isotactic Polystyrene/Phenylene Oxide Copolymer Blends.

homopolymers corresponding to the constituents of a copolymer are not individually miscible with a given homopolymer yet the copolymer is miscible. For example, styrene/acrylonitrile, SAN, copolymers are miscible with poly(methyl methacrylate) and with poly(ethyl methacrylate), yet neither polystyrene nor poly(acrylonitrile) is individually miscible with either of these methacrylates (42). Similarly, SAN copolymers are miscible with poly(ethyl oxazoline) (43), and with a variety of polyesters (44,45), and copolymers of ortho- and para- chlorostyrene are miscible with poly(phenylene oxide) (46), yet the corresponding homopolymers are immiscible with these materials. These examples could all be cases where all the B parameters are positive, as discussed above.

We have recently evaluated the interaction energies for miscible blends of isotactic polystyrene with copolymers of 2,6-dimethylphenylene oxide, comonomer 1, and 2,3,6-trimethylphenylene oxide, comonomer 2, provided by Borg-Warner Chemicals, by following the melting point depression of the crystallizable isotactic polystyrene, monomer unit 3, with increasing volume fractions of copolymer in the blends (47). The results, obtained after extensively annealing the blends and employing the Hoffman-Weeks analysis (48), are indicative of still another example of copolymer miscibility with a homopolymer, see Figure 4. The interaction parameter for the copolymer with the polystyrene is seen to be negative throughout the range of copolymer compositions studied, in agreement with the miscibility observed, and to vary in a concave downward manner with increasing comonomer 2 content. With reference to equation (8), this suggests that B_{23} is more negative than B_{13} , and that B_{12} is also negative. Unfortunately, the range of copolymer compositions is too limited to draw any further conclusions regarding the magnitudes of the B_{ij} parameters.

Ternary Blend Phase Behavior Only two partially miscible ternary polymer blends were reported prior to 1985 (49,50), although seven new miscible and partially miscible systems were reported

in 1986 (50-53) as interest in these more complex materials began to develop. Most of the miscible ternary systems reported to date were discovered by using the known miscibility of polymer binaries to find polymeric solvents to solubilize an immiscible binary pair; that is, polymers A and B may not be miscible, however each is miscible with polymer C, and addition of sufficient C to A and B leads to a miscible ternary composition.

The binary interaction model, equation (4), has been employed, with fair success, to explain and describe the phase behavior of some of these ternary systems (51,54). As in the case of binary mixtures, miscibility is directly linked to the presence in the blend of an exothermic heat of mixing, and $\Delta H_{\text{mix}} = 0$ becomes the criterion for predicting a boundary between single phase and multiphase behavior. Provided only one of the ternary components, component 2, is crystallizable, the melting point depression of this component in the miscible binary mixtures with each of the other blend components and in the miscible portion of the ternary compositions becomes a convenient way to determine the B_{1j} parameters needed to predict the boundary.

For the ternary mixture, the partial molar enthalpy of component 2, ΔH_2 , becomes

$$\Delta H_2 = 3\Delta H_{\text{mix}}/3n_2 = V_2 (B_{12}\phi_1^2 + B_{23}\phi_3^2 + \Delta B\phi_1\phi_3) \quad (9)$$

where,

$$\Delta B = B_{12} + B_{23} - B_{13} \quad (10)$$

V_2 is the molar volume of the repeat unit of component 2, and ϕ_1 is the volume fraction of polymer component 1 in the mixture. The melting temperature in the blend is then found, in the high molecular weight limit, by equating ΔH_2 to the difference in partial molar enthalpies between the crystalline polymer structural unit and that same unit in the hypothetical pure liquid state (1) to obtain (51),

$$T_m = T_m^0 (1 + (\Delta H_2/V_2)(v_{2u}/\Delta h_{2u})) \quad (11)$$

where $(\Delta h_{2u}/v_{2u})$ is the heat of fusion per unit volume of crystalline unit 2, T_m the melting temperature in the blend, and T_m^0 the melting temperature in the pure state. Combining equations (9), (10), and (11) yields

$$T_m = T_m^0 (1 + B(v_{2u}/\Delta h_{2u})(1 - \phi_2)^2) \quad (12)$$

where,

$$B = B_{12}\theta_1^2 + B_{23}\theta_3^2 + \Delta B\theta_1\theta_3 \quad (13)$$

$$\theta_1 = \phi_1/(1 - \phi_2)$$

Equation (12) has the same form as that commonly used to evaluate B from the melting point depression component 2 in a miscible binary (4,5) and will reduce to that form if either ϕ_3 or ϕ_1 is zero. Consequently the same experimental procedures can be used to obtain B in both binary and ternary systems. The B parameter obtained in a miscible ternary, however, is a function of all three binary interaction parameters and weighted by the volume fractions of amorphous materials, θ_1 , in the ternary. The unknown parameter, B_{13} , for the immiscible binary pair, can be obtained from analysis of the curve B vs. θ_1 through equation (13).

An example of this construction is shown in Figure 5 for the miscible region of the ternary blend of polycarbonate, 1, poly(ϵ -caprolactone), 2, and Phenoxy, 3 (54). Components 1 and 2 form a miscible binary as do components 2 and 3, and both B_{12} and B_{23} are negative, as expected, and B_{23} is more negative than B_{12} , perhaps as a result of the strong interaction between the OH functionality of 3 and the carbonyl ester of 2 (28). Components 1 and 3 are immiscible, and B_{13} is found to be +4.6 cal/cc from a

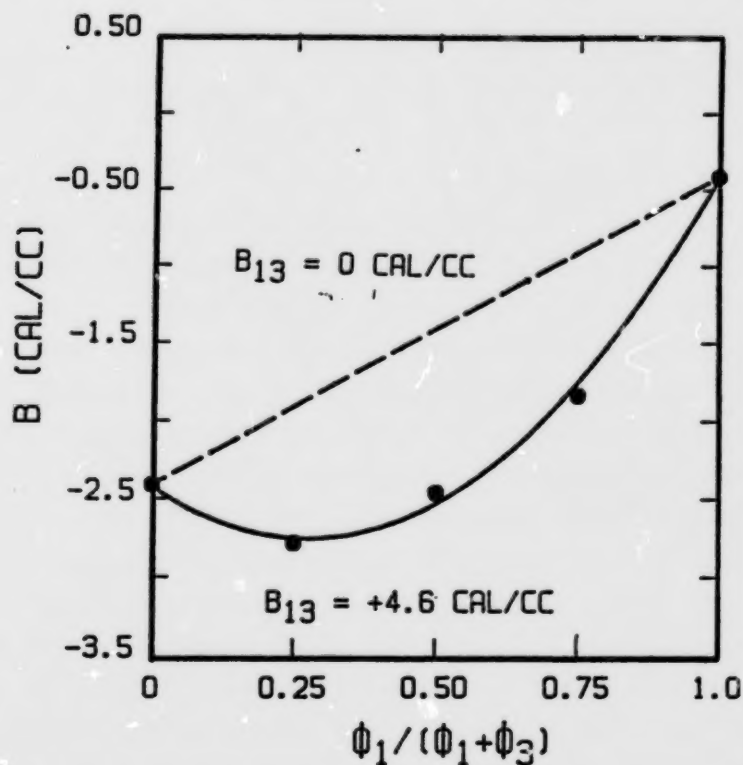


Figure 5. Variation of Interaction Parameter with the Fraction of Polycarbonate in the Amorphous Portion of the Miscible Ternary Blend of Polycarbonate/Phenoxy/Poly(ϵ -caprolactone).

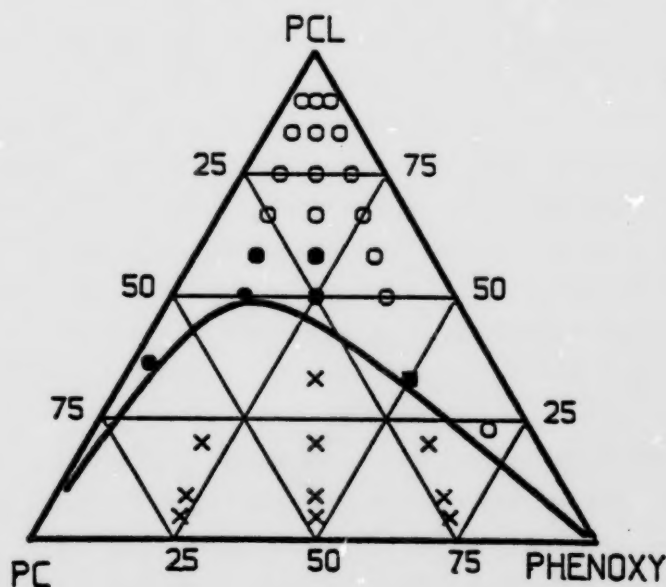


Figure 6. Comparison of Calculated with Observed Regions of Miscibility. (x) indicates two T_g 's and cloudy melt. (O) indicates one T_g and clear melt. (●) indicates one T_g and cloudy melt.

curve fit of the data to equation (13).

The miscibility boundary for this ternary, calculated with equation (4), the B_{1j} parameters from Figure 5, and the assumption that $\Delta H_{mix} = 0$ defines the boundary between miscible and immiscible behavior is shown in Figure 6 to do a reasonable job of predicting the state of miscibility, as observed from both optical and glass transition temperature measurements. Both the data and the calculation suggest that more of the poly(ϵ -caprolactone) solvent is required to solubilize polycarbonate-rich compositions, relative to Phenoxy-rich blends, a conclusion that seems to verify the assumption that $\Delta H_{mix} \leq 0$ is required for both binary and multicomponent polymer blend miscibility.

GROUP CONTRIBUTION METHODS FOR PREDICTING BLEND MISCIBILITY

Since enthalpic interactions are primarily determined by nearest neighbor interactions, it is possible to gain some nearly quantitative insight into the molecular structural features required for miscible blend formation by measuring the heats of mixing of low molecular weight analogs of the polymer blend component repeat units. While this technique has enjoyed good success in a variety of studies (12,32,34,55-60), its utility critically depends on how closely the analogs selected actually simulate the interactions of the polymers. For example, polymeric structural features such as stereoregularity (60-62) and perhaps sequence distribution in copolymers can strongly influence polymer-polymer miscibility, yet are difficult to simulate in analog calorimetry measurements. It is also often difficult to find suitable low molecular weight analogs for many of the structural groups commonly seen in many polymeric materials. Even when these are found, the measured heats of mixing may not follow the composition dependence suggested by the simple van Laar form of equation (2). These problems can be partially resolved by the use of modern thermodynamic theories which employ group contribution methods to obtain characteristic interaction parameters for basic structural groups which are

present in both the polymer repeat unit and in the analog.

Basically any thermodynamic model which calculates the heat of mixing in terms of group interactions could serve as a group contribution method. One of the more widely practiced and recognized methods in chemical engineering is the Universal Quasichemical method, UNIQUAC (63), which is a solution of functional groups concept based on modifications to the earlier quasichemical model of Guggenheim (64,65). One of the chief virtues of UNIQUAC and the related UNIFAC methods (66,67), outside of fitting thermodynamic data fairly well, is that a large number of functional groups have been characterized from thermodynamic data on liquid mixtures. Its chief disadvantage is a certain awkwardness of form which results from the "two fluid" assumption of the local fluid microstructure. A conceptually somewhat cleaner extension of Guggenheim's original theory has been developed by Panayiotou and Vera (68), and our own work in this area, with the exception of an additional modification, mentioned below, closely follows their development.

All quasichemical theories assume that the local composition of structural groups can be different from the average composition in the mixture and that this deviation is related to the energy of the i - j contact pair,

$$\frac{N_{ij}^2}{4N_{ii}N_{jj}} = A_{ij} \exp(-2\Delta E_{ij}/kT) \quad (14)$$

$i, j = 1 \text{ to } f, i \neq j$

where N_{ij} is the number of i - j contacts, f is the number of different groups in the system, and ΔE_{ij} is the i - j contact or exchange energy,

$$\Delta E_{ij} = E_{ij} - 1/2E_{ii} - 1/2E_{jj} \quad (15)$$

The pre-factor, A_{ij} , in equation (14) is taken to be unity in the

Guggenheim theory. We have permitted the prefactor in our work because its presence leads to improved fits of liquid heats of mixing. The rationale for including it is an assumption that the local equilibrium expressed by equation (14) should be replaced by a true chemical equilibrium, in which case the equilibrium constant should follow the free energy, ΔF_{ij} , and

$$A_{ij} = \exp(2\Delta S_{ij}/k) \quad (16)$$

Each i-j contact type is clearly characterized by two parameters, ΔE_{ij} and A_{ij} , in our model.

The number of contact pairs, N_{ij} , can be related to the numbers and types of groups through a variety of approximations. The most common method (63-68) considers each group i to have zq_i nearest neighbors where $z=10$ is the coordination number, and q_i is a parameter proportional to the group's external surface area,

$$q_i = A_{wi}/(2.5 \times 10^9) \quad (17)$$

The numerical factor in equation (17) is the standard segment area of a methylene group, cm^2/gmole , and A_{wi} is the area of the molecule given by Bondi (70). The average area fraction of n_i groups of type i in the mixture is then given by

$$\phi_i = q_i n_i / (\sum_j q_j n_j) \quad (18)$$

Guggenheim (65) has shown that this average area fraction can be related to the number of contacts in a totally random, athermal, mixture by

$$x_{ij} = x_{ji} = z(\sum_k q_k n_k) \phi_i \phi_j \quad (19)$$

$$x_{ii} = (z/2)(\sum_k q_k n_k) \phi_i^2$$

The numbers of contact sites for the locally non-random mixture

can be obtained from the totally random numbers by

$$N_{ij} = N_{ji} = \Gamma_{ij} X_{ij} = \Gamma_{ji} X_{ji} \quad (20)$$

$$N_{ii} = \Gamma_{ii} X_{ii}$$

where Γ is the non-random parameter of Panayiotou and Vera (68), $\Gamma_{ij} = \Gamma_{ji}$, and where

$$\sum_j \psi_j \Gamma_{ji} = 1 \quad (21)$$

is required by the conservation of contact sites for each group i . Provided A_{ij} and ΔE_{ij} are known, the non-random parameters, Γ_{ij} can be evaluated for each i - j pair by eliminating Γ_{ii} through equation (21), and by combining equations (19), (20), and (14),

$$\frac{\Gamma_{ij}^2 \psi_i \psi_j}{(1 - \sum_{j \neq i} \psi_j \Gamma_{ij})(1 - \sum_{i \neq j} \psi_i \Gamma_{ij})} = A_{ij} \exp(-2\Delta E_{ij}/kT) \quad (22)$$

The heat of mixing of groups is then given, in terms of contact sites by

$$\begin{aligned} \Delta H_{\text{mix}} &\approx \Delta U_{\text{mix}} = \sum_i \sum_{j>i} N_{ij} \Delta E_{ij} \\ &= (\sum_k z_k q_k n_k) \sum_i \sum_{j>i} \Gamma_{ij} \Delta E_{ij} \psi_i \psi_j \end{aligned} \quad (23)$$

Equation (23) is similar, in form, to the binary interaction model, equation (4). Reasoning, similar to that used to develop equation (5), can be employed to give

$$\Delta H_{\text{mix}}/V = \sum_i \sum_{j>i} B_{ij}' \psi_i \psi_j - \sum_k \psi_k B_{ij}',^{(k)} \psi_i^{(k)} \psi_j^{(k)} \quad (24)$$

for the heat of mixing of the component molecules where,

$$B_{ij}' = S \Gamma_{ij} \Delta E_{ij} \quad (25)$$

Table 1. Summary of Correlation with Quasichemical Method

Interacting Groups, ij	No. of Systems	Data Points	A_{ij}	ΔE_{ij} cal/gmole	Pct. RMS Error
$\text{CH}_2/\text{CH}_2\text{COO}$	9	123	1.00	137.4	10
$\text{CH}_2/\text{CH}_2\text{Cl}$	7	83	0.501	88.3	11
$\text{CH}_2\text{Cl}/\text{CH}_2\text{COO}$	2	14	4.76	19.4	18

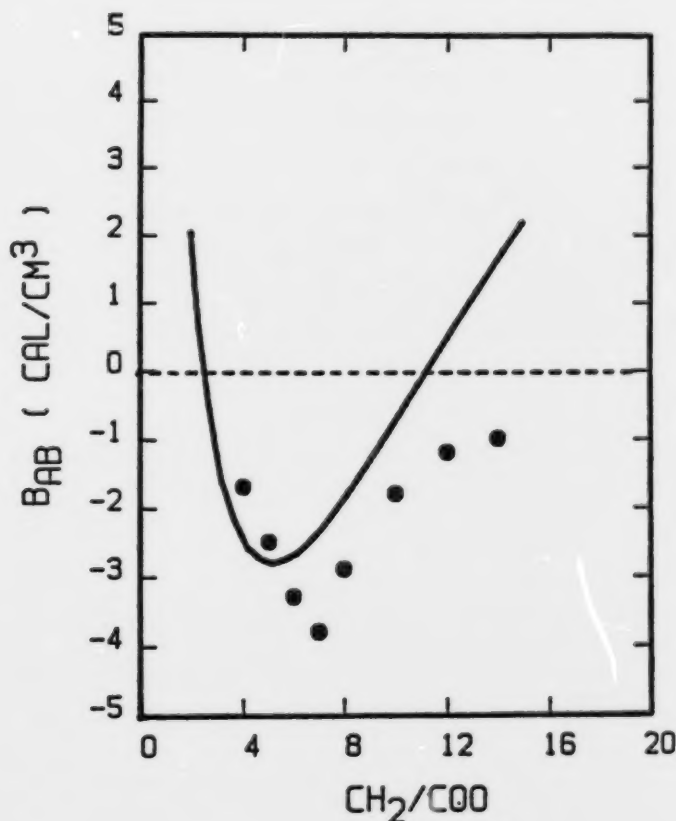


Figure 7. Comparison of Calculated Interaction Parameters from Quasichemical Theory and Liquid Heats of Mixing with Observed Interaction Parameters in PVC/Polyester Blends.

$$B_{ij}^{(k)} = S^{(k)} r_{ij}^{(k)} \Delta E_{ij}$$

and S and $S^{(k)}$ are the number of contact sites per unit volume of the mixture and of pure component k , respectively, given by,

$$S = z \sum_k n_k q_k / V \quad (26)$$

$$S^{(k)} = z \sum_m n_m^{(k)} q_m^{(k)} / V^{(k)}$$

Table 1 summarizes the interaction parameters found by fitting equations (24) and (22) to liquid heats of mixing data of ester/alkane (70-72), chlorinated hydrocarbon/alkane (73-78), and dichlorobutane/ester (79) systems. As suggested by the parameters in the table, we have considered the important group interactions to be only $\text{CH}_2/\text{CH}_2\text{COO}$, $\text{CH}_2/\text{CH}_2\text{Cl}$, and $\text{CH}_2\text{Cl}/\text{CH}_2\text{COO}$. The parameters are obtained by use of a non-linear curve-fitting technique. Generally, we are able to fit experimental data to within relative errors of less than 20% with this correlation scheme. It is interesting to note that all of the ΔE_{ij} parameters are positive, but that groups which can interact strongly, such as the $\text{CH}_2\text{Cl}/\text{CH}_2\text{COO}$ group, show smaller ΔE_{ij} values than groups which interact weakly, or endothermically.

The whole point of this activity is to be able to predict polymer-polymer miscibility with group interaction parameters which have been determined from liquid heats of mixing data bases. One example of this ability is shown in Figure 7 which compares the calculated variation with ester structure of the overall interaction parameters for poly(vinyl chloride)/aliphatic polyester blends with experimental values obtained from melting point depressions of the polyesters. The curve is calculated using the ΔE_{ij} and A_{ij} parameters in Table 1, and is seen to predict nearly the same "miscibility window", $B < 0$, as is observed experimentally. The prediction is obviously not perfect, perhaps for some of the reasons stated at the beginning of this section as well as the data bases and model employed, but it does represent an important beginning toward predicting

polymer-polymer miscibility with modern thermodynamic theories for liquid mixtures.

ENTHALPICALLY DRIVEN VAPOR SORPTION IN POLYMERS

The use of polymer coatings on mass sensitive resonators for detecting very low solvent vapor concentrations in air is an emerging technology whose success depends critically on the enthalpic interactions between the polymer and the solvent vapor. Resonators, such as piezoelectric crystals (80-82), surface acoustic wave, SAW, devices (80,83,84), and mechanical tuning forks, show a shift in resonant frequency which is proportional to the change in mass of the device and proportional to the square of the operating frequency (82). Even high frequency devices are limited in their ultimate sensitivity, however, by the thermodynamic partitioning of solvent vapor into the detector coating.

A simple analysis, valid in the limit of very low sorption in the polymer, is provided by the Flory-Huggins theory (1),

$$\phi_1 = (P_1/P_1^0) \exp[-(1 + x_{12})] \quad (27)$$

where ϕ_1 is the equilibrium volume fraction of solvent in the polymer, P_1 the partial pressure of solvent vapor, P_1^0 the saturation vapor pressure of pure solvent at the system temperature, and x_{12} the interaction parameter between polymer and solvent. Equation (27) clearly suggests that greatest sorption in the polymer will occur if the polymer is designed to have a large negative interaction parameter with the solvent of interest. According to equations (2) and (3), this is equivalent to saying that strong partitioning of solvent in the polymer phase can be expected if ΔH_{mix} of the solvent and polymer segments is exothermic. The problem of finding sensitive polymer coatings thus reduces to an exercise in analog calorimetry and thermodynamics.

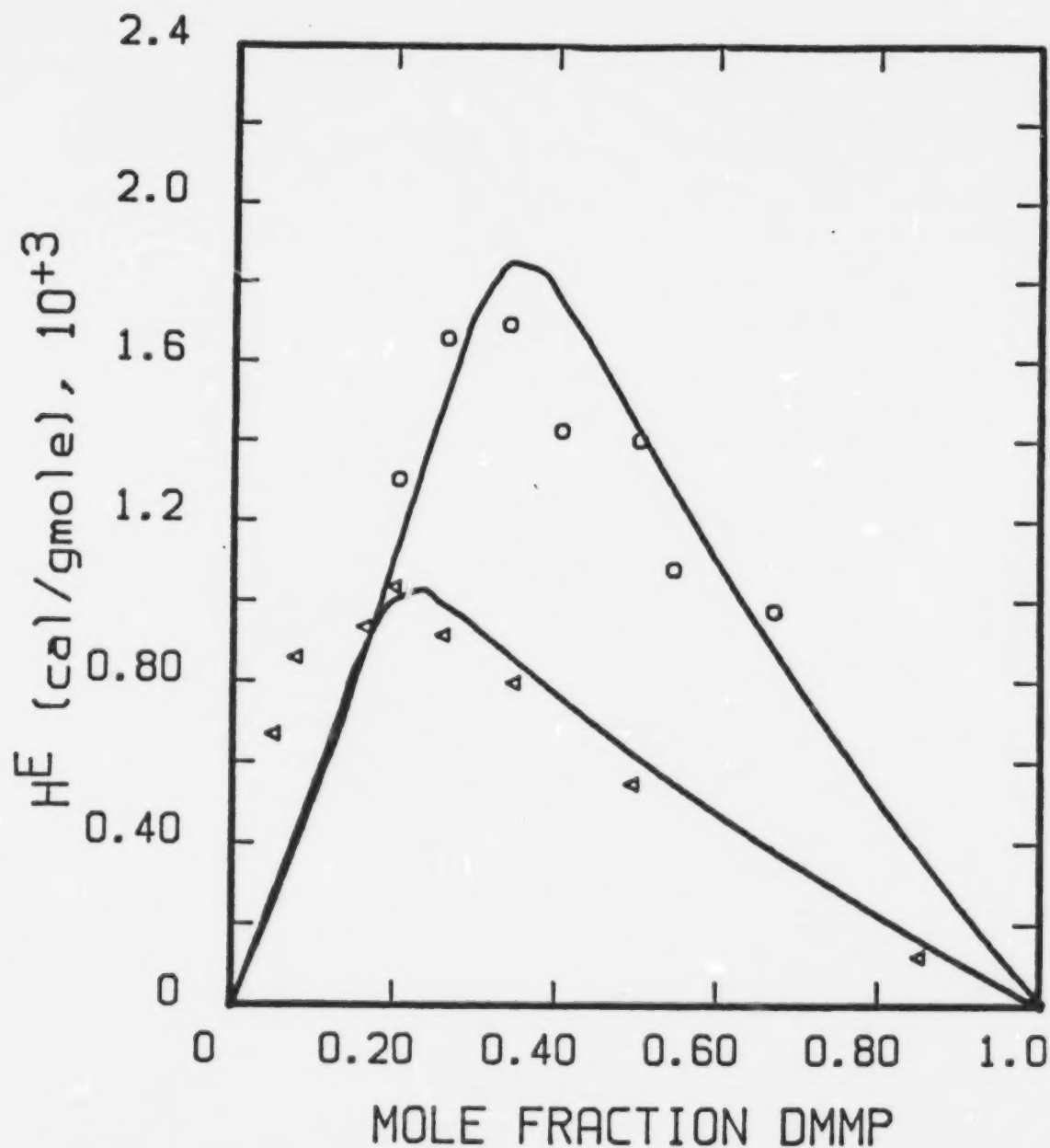


Figure 8. Heats of Mixing of HFIP/Ethyl Benzene Solutions with DMMP at 25 °C. (e) 0.5 mole fraction HFIP in Ethyl Benzene (Δ) 0.25 mole fraction HFIP. Solid Lines are Calculated with $K = 21$ liters/gmole and $\Delta H^0 = -6500$ cal/gmole.

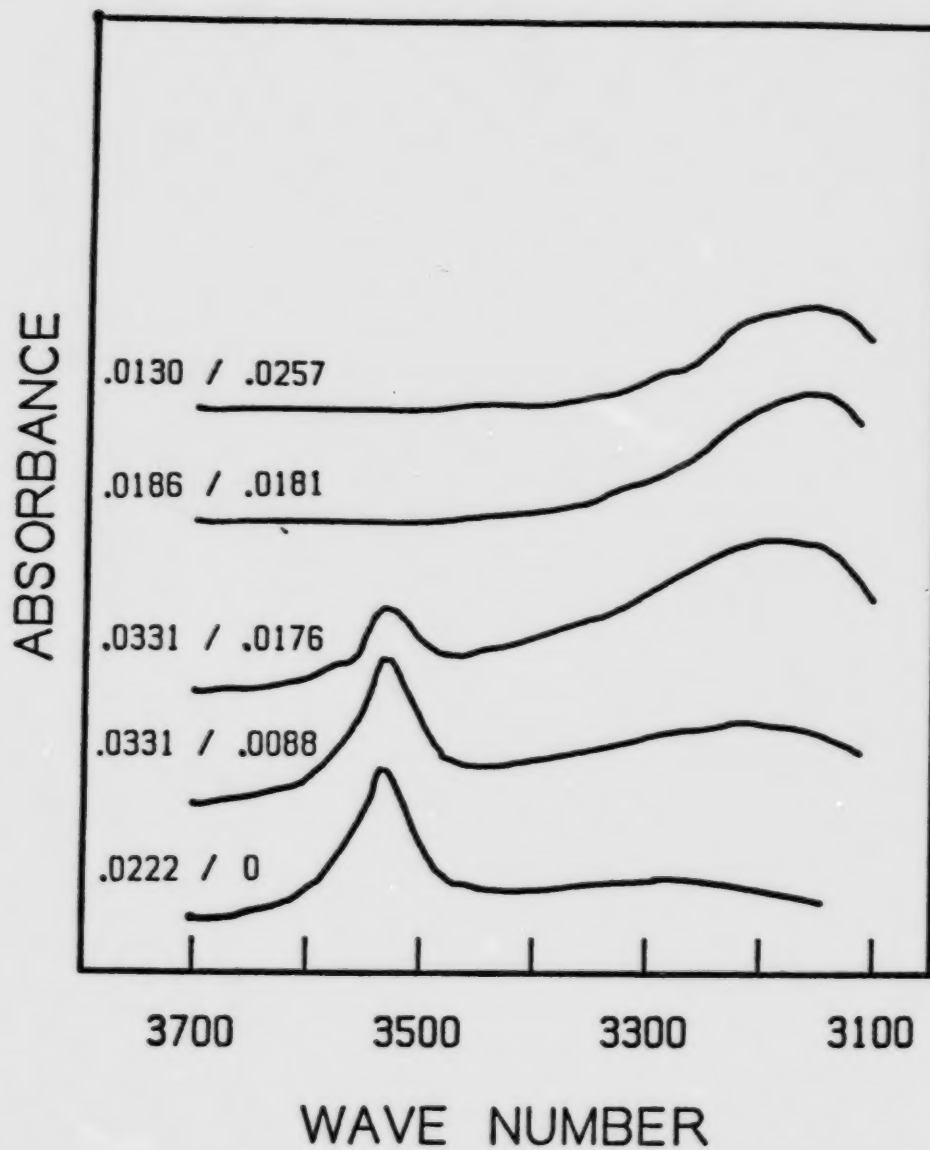


Figure 9. Infrared Absorbance Spectra For Various Initial Mole Fractions HFIP/DMMP in Ethyl Benzene at 25 °C.

Our laboratory recently completed a program in which polymer coatings for strongly sorbing dimethyl methyl phosphonate, DMMP, a non-toxic analog of certain chemical warfare agents and insecticides, were developed (85,86). Heats of mixing measurements were made for DMMP with a variety of liquids. These results indicate that coatings which contain chemical moieties with acidic hydroxyls, such as phenols and fluoroalcohols, should be good sorbers of the basic phosphorus ester. Hexafluoroisopropanol, HFIP, seemed to be particularly attractive because of its highly exothermic interaction with DMMP and because its analog, the hexafluorocarbon moiety, could be easily grafted on the aromatic rings of polystyrene by the reaction of hexafluoroacetone in the presence of aluminum chloride and subsequently hydrolyzed to the alcohol.

The effect of copolymer composition sorption of DMMP was simulated by mixing DMMP with solutions containing varying amounts of hexafluoroisopropanol with ethyl benzene, the analog for the styrene repeat unit. As indicated by Figure 8, ΔH_{mix} was always found to be most exothermic at compositions corresponding a 1:1 molar equivalence of DMMP to HFIP, indicating a very strong interaction. Further examination of the solutions by FTIR showed that the OH peak absorbance of the HFIP at 3550 cm^{-1} disappears and that a new absorbance peak at roughly 3200 cm^{-1} when DMMP is added to HFIP/ethyl benzene solutions, Figure 9. This behavior is consistent with the formation of a hydrogen bond between HFIP and DMMP (87,88). The equilibrium constant, K, for the formation of the 1:1 hydrogen bond,



$$K = \frac{[C]}{[A][B]} = V \frac{n_C}{(n_A - n_C)(n_B - n_C)} \quad (28)$$

where [A] is the equilibrium molar concentration and n_A the initial moles, respectively, of HFIP, [B] and n_B that for DMMP,

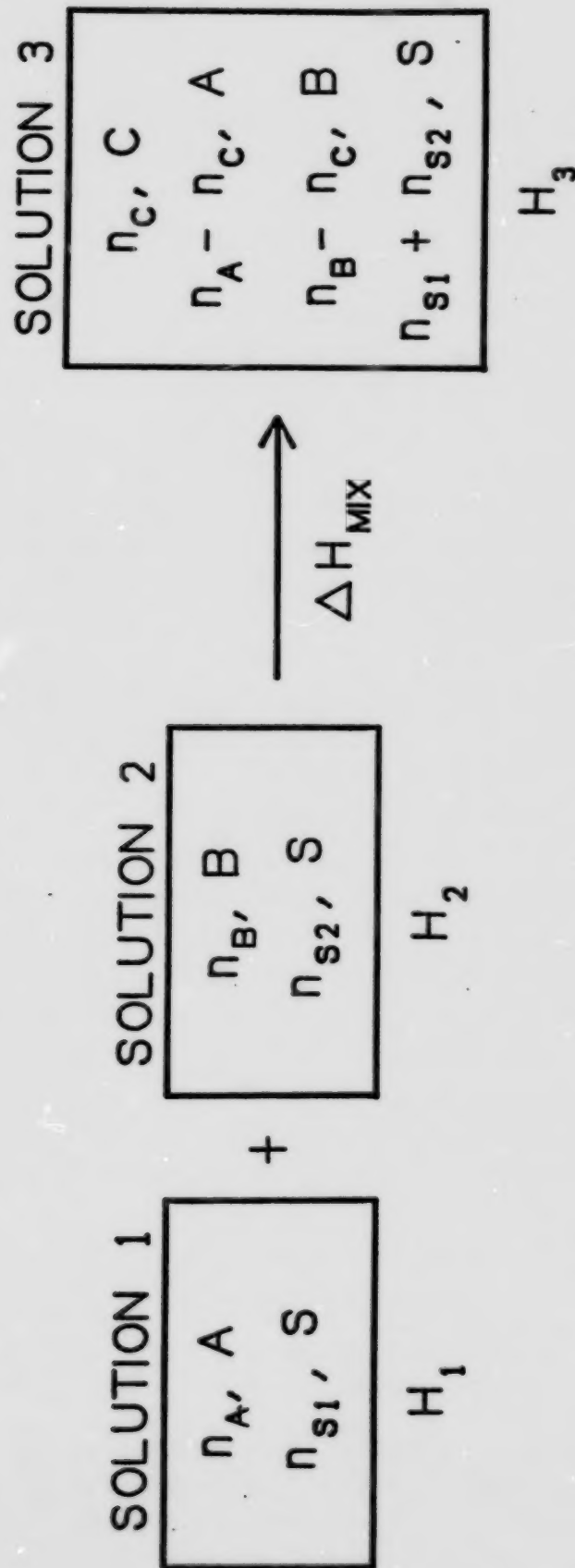


Figure 10. Schematic for Calculating the Heat of Mixing for Strongly Interacting Fluids.

and $[C]$ and n_C that of the complex formed, was found to be 21 liters/gmole at 25 °C by application of the Hildebrand-Benesi (89) method to the spectra.

This information was then used to write a general model for ΔH_{mix} of the strongly interacting system, shown schematically in Figure 10. The solution enthalpies, H_1 , in this figure can be evaluated relative to the elements through heats of formation and heats of mixing terms; for example,

$$H_1 = n_A H_{fA}^0 + n_{S1} H_{fS}^0 + \Delta H_1 \quad (29)$$

where ΔH_1 is the heat associated with mixing n_A moles of pure A with n_{S1} moles of pure solvent and H_{fA}^0 and H_{fS}^0 are the heats of formation of A and S. The terms ΔH_1 can be evaluated using the Hildebrand and Scott solubility parameter approach (90), by using experimental heats of mixing data for DMMP/ethyl benzene and HFIP/ethyl benzene mixtures, and the known solubility parameter for ethyl benzene to establish δ_A , δ_B , and δ_S . This is possible because the experimental heats of mixing of reactants with solvent are endothermic or regular. The solubility parameter for the complex, δ_C , must be estimated because the complex can not be isolated. Following the usual procedure (90), this is done by treating the complex as a solution of A and B,

$$\delta_C = \phi_A \delta_A + \phi_B \delta_B \quad (30)$$

where ϕ_1 is the volume fraction of 1 in the complex. By also defining a mean solubility parameter for each of the solutions 1, 2, and 3, for example,

$$\delta_1 = \phi_{A1} \delta_A + \phi_{S1} \delta_S \quad (31)$$

where ϕ_{11} is the volume fraction of component 1 in solution 1, the heat of mixing with complex formation becomes,

$$\Delta H_{\text{mix}} = H_3 - H_1 - H_2 \quad (32)$$

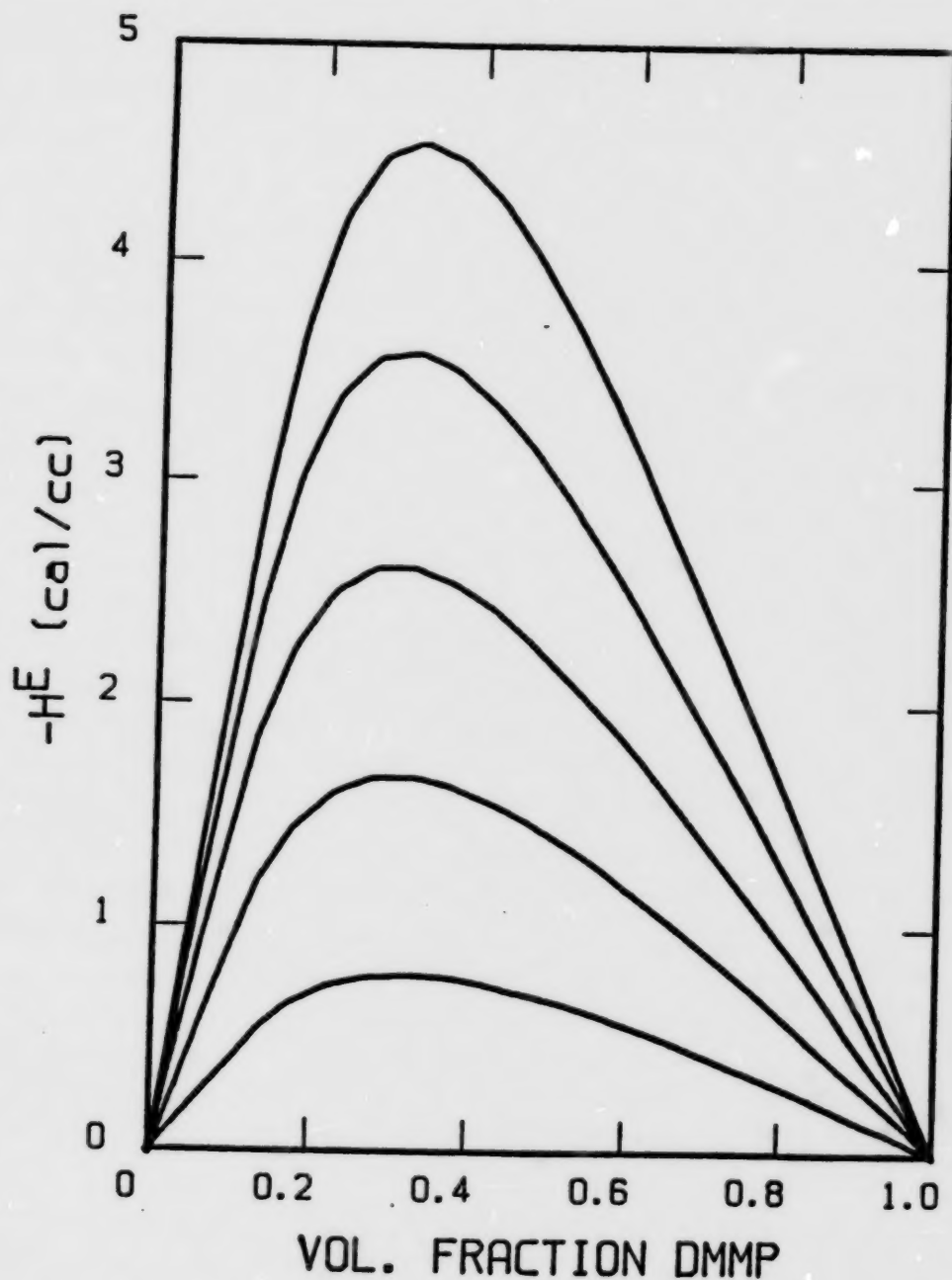


Figure 11. Calculated Heats of Mixing for HFIP/Ethyl Benzene Solutions with DMMP at 135 °C. Mole Fractions HFIP in Ethyl Benzene vary from 0.25 (top curve) to 0.05 (bottom curve) in 0.05 increments.

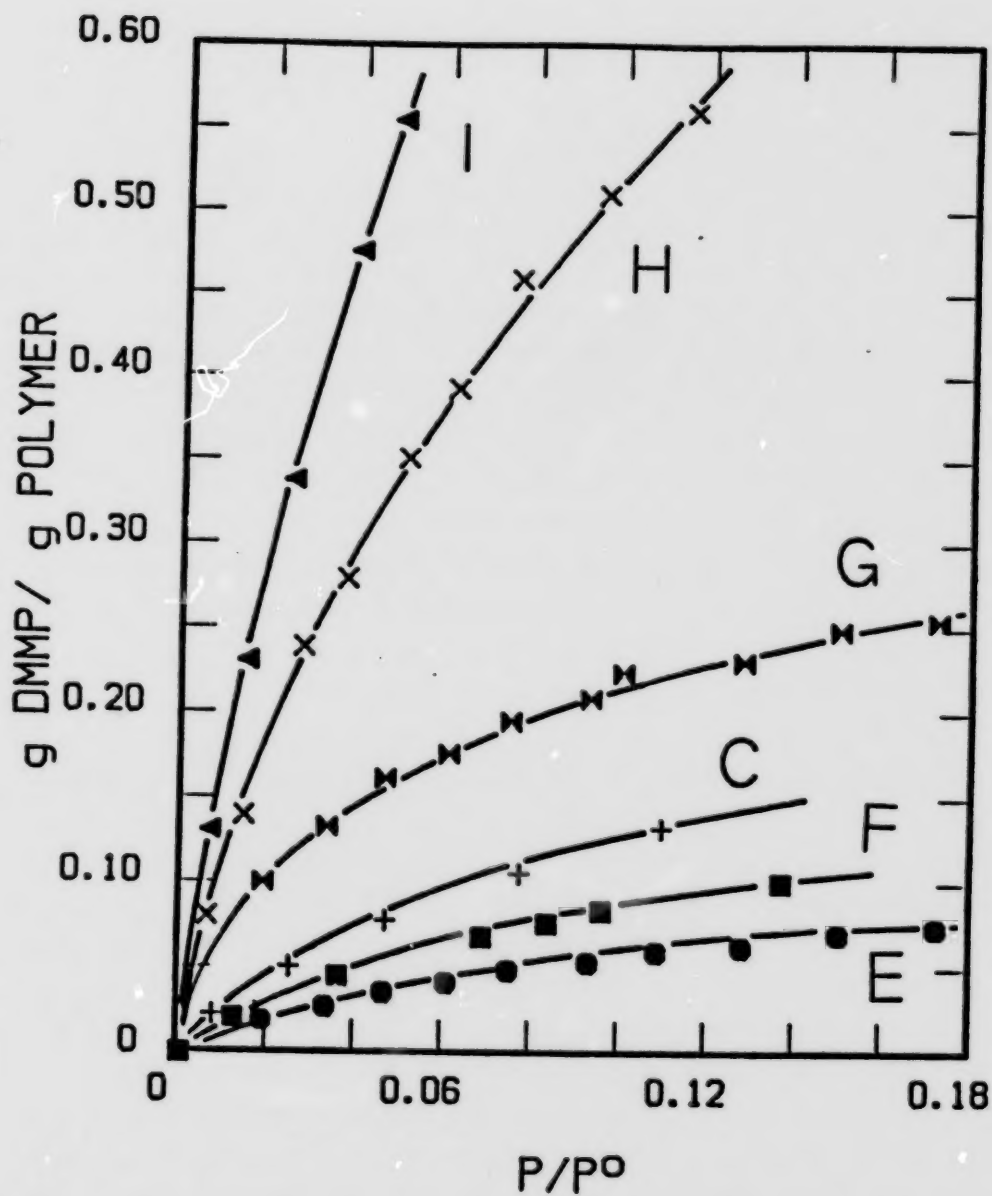


Figure 12. Sorption Isotherms at 135 °C for DMMP Vapor in Hexafluorocarbonol Substituted Styrene Copolymers. Substitutions are: (I) 54%, (H) 41%, (G) 31%, (C) 17%, (F) 12%, (E) 2.4%.

$$\begin{aligned}
&= n_C \Delta H^0 + n_C [V_C (\delta_C - \delta_3)^2 - V_A (\delta_A - \delta_3)^2 - V_B (\delta_B - \delta_3)^2] \\
&+ n_{S1} V_S [(\delta_S - \delta_3)^2 - (\delta_S - \delta_1)^2] + n_{S2} V_S [(\delta_S - \delta_3)^2 - (\delta_S - \delta_2)^2] \\
&+ n_A V_A [(\delta_A - \delta_3)^2 - (\delta_A - \delta_1)^2] + n_B V_B [(\delta_B - \delta_3)^2 - (\delta_B - \delta_2)^2]
\end{aligned}$$

where, $\Delta H^0 = H_{fC}^0 - H_{fB}^0 - H_{fA}^0$ is the heat of reaction per mole of complex formed in the standard state. With the exception of ΔH^0 , all of the parameters in equation (32) are known or calculable from experimental observations. As suggested by the solid lines in Figure 8, the use of $\Delta H^0 = -6500$ cal/gmole with equations (32) and (28) gives a reasonable prediction of ΔH_{mix} . Although not shown here, this value and the model does a very good job of predicting heats of mixing over a wide range of solution concentrations and over temperature changes from 4 °C to 35 °C (86), via the well known relationship (91),

$$K_2 = K_1 \exp[(\Delta H^0/R)(1/T_1 - 1/T_2)] \quad (33)$$

Figure 11 shows some calculated heats of mixing of pure DMMP with HFIP/ethyl benzene solutions at 135 °C, where K is reduced to 1.09 liters/gmole by equation (33). Due to this lower K value, the locations of the maxima are less sharply defined than those in Figure 9, yet the maxima still occur where the DMMP and HFIP are stoichiometrically balanced. These calculated curves do not follow the parabolic composition dependency implicit in equation (27); stated another way, these calculations suggest that the Flory-Huggins Chi parameter for sorption of DMMP by the copolymer will depend not only on the copolymer composition but on the concentration of DMMP sorbed in the copolymer.

Figure 12 shows equilibrium sorption isotherms for DMMP in copolymer melts, measured by the piezoelectric method at 135 °C, for 0.5 micron coatings on a 7 MHz crystal. Equilibrium, particularly at low vapor activities, takes typically 5 to 10

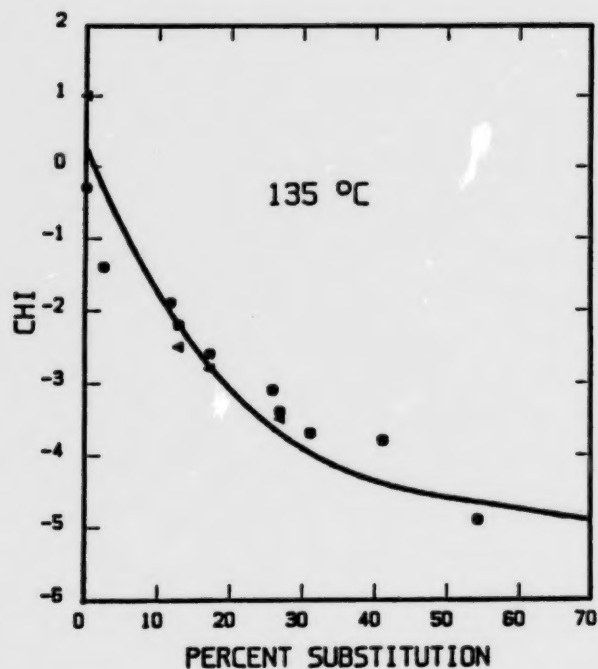


Figure 13. Comparison of Predicted Interaction Parameters, χ , with Experimental Values from Piezoelectric Sorption (e) and from Inverse Gas Chromatography (A).

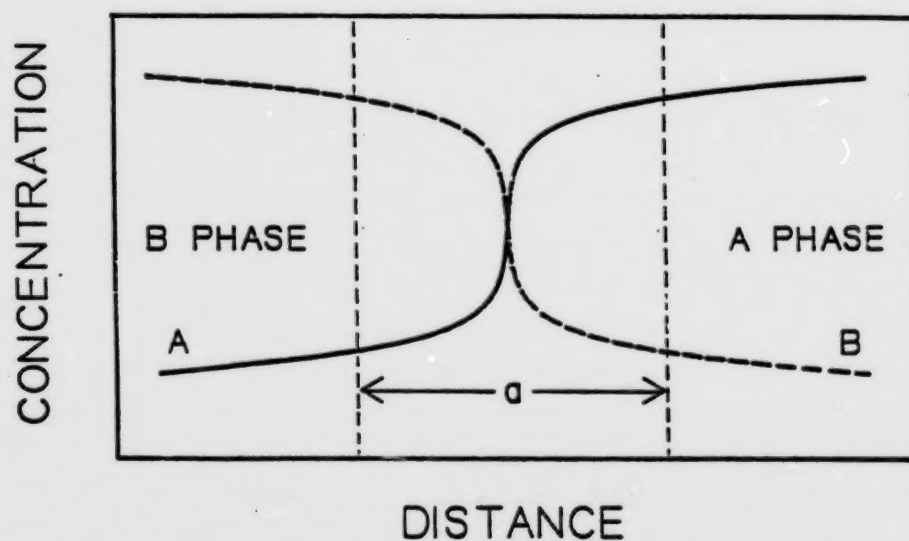


Figure 14. Schematic of Interfacial Zone.

hours to achieve (86). The slope of each isotherm decreases with increasing DMMP concentration, and the slope of each isotherm, at very low DMMP levels, increases nonlinearly with increasing hexafluorocarbonol content in the copolymer. These observations are consistent with the predictions of the heat of mixing, Figure 11. Despite the non-linearities in each isotherm, one can determine an experimental x_{12} by fitting equation (27) to the linear portion of each isotherm at low DMMP concentration. One can also determine a predicted x_{12} by fitting equations (2) and (3) to the low DMMP regions of the predicted heats of mixing, Figure 12.

Figure 13 shows a comparison of the experimental and predicted x_{12} values as a function of the percent of aromatic rings of polystyrene which are substituted with hexafluorocarbonol. Also included are some x_{12} values determined by Inverse Gas Chromatography (86). Agreement between experiments and theory is quite good, thus indicating the potential value of spectroscopic and thermodynamic analysis of ΔH_{mix} of analog compounds for predicting hydrogen bond driven vapor sorption in polymers.

ENTHALPIC INTERACTIONS AND ADHESION IN POLYMERIC SYSTEMS

Even when the interactions between polymer blend components are weak and the resulting composition is immiscible, the mechanical properties of the mixture may still depend on enthalpic interactions and related polymer-polymer adhesion between the phases (92,93). As reviewed by Wu (94,95), local or segmental diffusion across the interface between blend components is required to achieve a good adhesive bond. The degree to which this can occur depends primarily on the enthalpic interaction between phases. Statistical thermodynamics theories predict that varying degrees of interdiffusion of polymer segments, depicted in Figure 14, will occur in the interfacial layer as required to minimize the interfacial energy (96-99). These theories predict that the characteristic interfacial thickness, a , is related to

the Flory-Huggins interaction parameter, x_{AB} , by,

$$a = c/(x_{AB})^m \quad (34)$$

where c and m are slightly different constants depending on the assumptions in the derivations (95-97). Equation (34) clearly suggests that the interfacial thickness and the strength of the interfacial bond increases as x_{AB} is lowered toward zero or, equivalently, as the blend components become nearly or partially miscible. This suggestion seems to be verified experimentally by a study of lap shear adhesion strengths for laminates prepared from highly immiscible, partially miscible, and miscible components (93).

Given the variety and complexity of phase morphologies and sizes that can result from different melt mixing and processing methods, it is difficult to quantitatively relate adhesion between phases, measured by a simple test such as lap shear, to the mechanical behavior of melt processed compositions. Qualitatively, however, the relationships seem clear: blend properties which are ductility related, such as elongation at break or impact strength, are very sensitive to the strength of the interface (93), and it is relatively easy to create a brittle blend from ductile but poorly adhering components. One mechanism by which this could occur is the generation of micro-cracks at the weak interface between phase domains at low levels of applied stress. The presence of micro-cracks would lead to very high localized stresses at the crack tips, with ensuing crack propagation and catastrophic mechanical failure at applied stress levels far below the strengths of the components (100). Studies, which use a stress dilatometer to simultaneously measure stress, strain, and volume change, are presently underway in our laboratory (101) to more carefully examine the role of interfacial adhesion on mechanical properties of melt processed, immiscible, blends.

An example of the qualitative relationships between

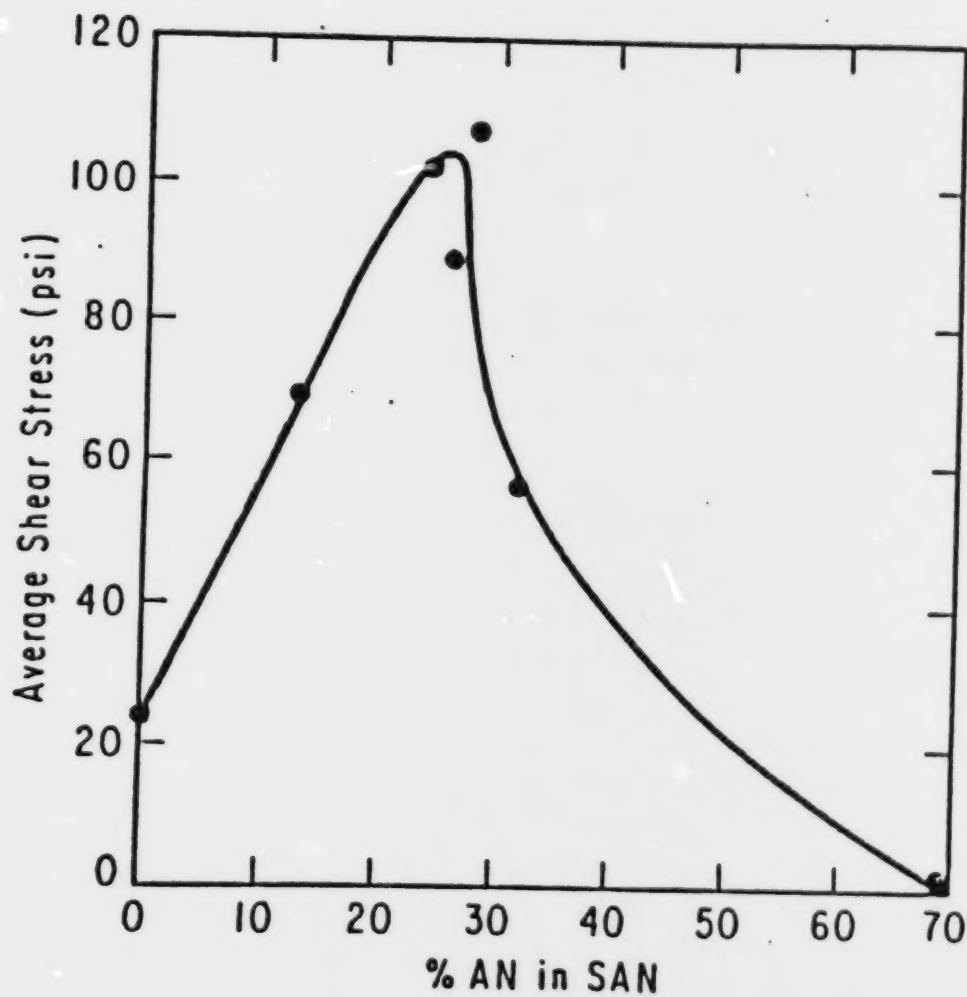


Figure 15. Effect of AN Content on Lap Shear Adhesion of SAN Copolymers to Polycarbonate (93).

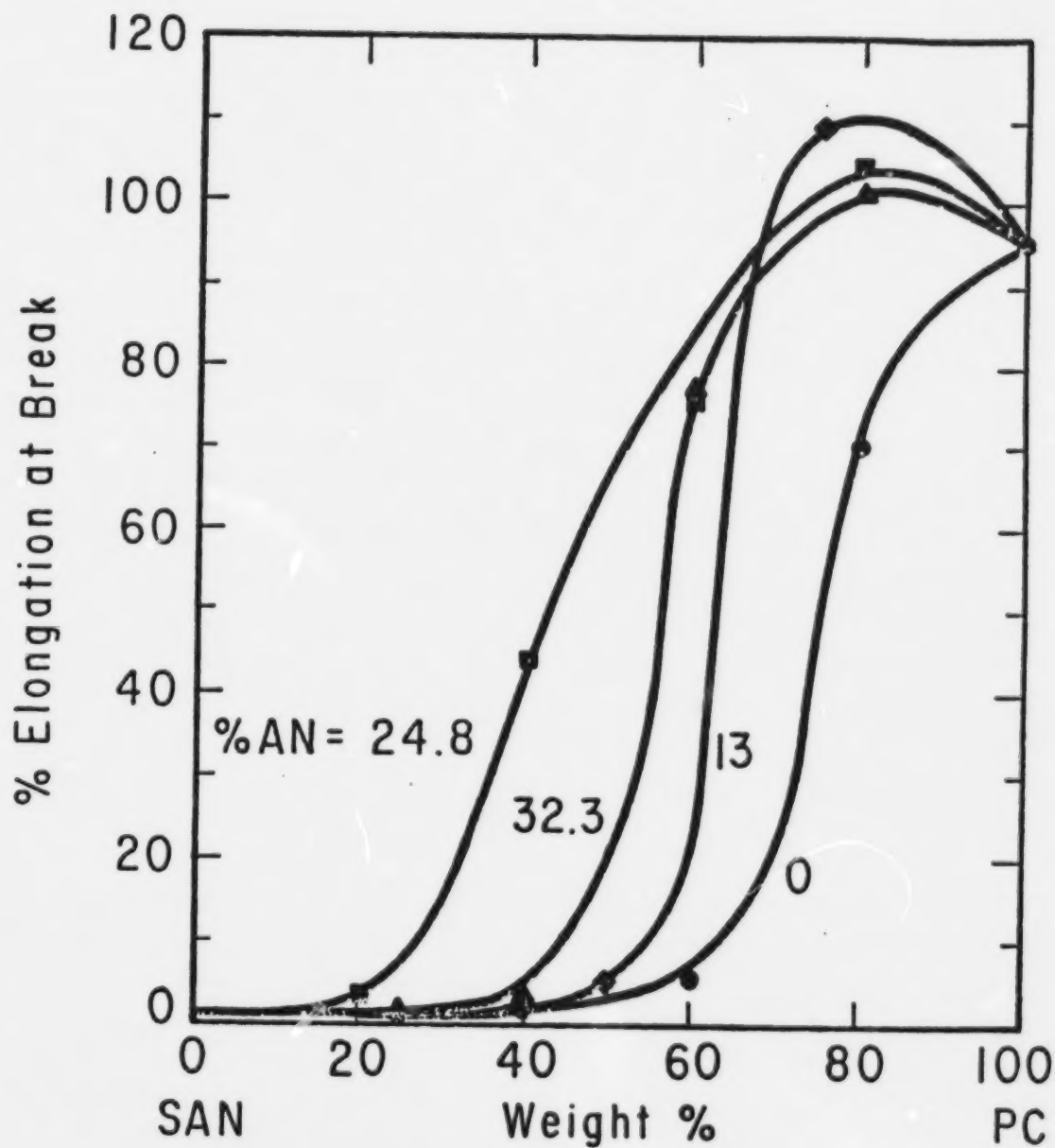


Figure 16. Influence of AN Content on Ductility Properties of Injection Molded SAN/PC Blends (93).

interfacial adhesion and blend ductility properties may be seen in Figures 15 and 16 for the poly(styrene-co-acrylonitrile), SAN, blends with polycarbonate, PC, in which the acrylonitrile content of the SAN has been varied (92). Lap shear measurements, Figure 15, show a maximum in the adhesion of SAN to PC when the AN content of the copolymer is near the azeotrope. At this composition, SAN is partially miscible with PC, as judged from T_g shifts of the blend phases, and this partial miscibility is probably responsible for the observed maximum in adhesion. SAN materials with either greater or lesser AN contents show both poorer adhesion and less partial miscibility with PC. The ductility of melt blended and injection molded compositions shows similar trends, Figure 16. Here, blends rich in SAN are brittle and compositions rich in PC are ductile, reflecting the properties of the continuous phase in each case. Adhesion between phases determines the efficiency of utilization of the ductile component properties. When adhesion is poor, brittle blend behavior extends into the PC continuous region. When adhesion is good, some blend ductility is retained even when the brittle SAN component is continuous.

Equation (34) suggests that the same enthalpic interactions responsible for immiscible blend formation can also be responsible for poor adhesion between the resulting phases and for brittle blend behavior. Consequently, researchers faced with the problem of achieving ductile blends from highly immiscible components have examined two alternate routes for increasing interfacial strengths. One of these routes involves chemically grafting materials on one of the components which are miscible with the other. For example, methyl methacrylate grafted olefins (102) are reported to be useful impact modifiers for poly(vinyl chloride), in part because PMMA is miscible with PVC, and numerous maleic anhydride grafted olefins (103-106) have been reported to impact modify nylon, probably through subsequent reaction reaction of the anhydride with the terminal amine of the polyamide. Typically, grafting reactions of this type can be carried out during the extrusion melt blending of the primary

components, using specially configured twin-screw extruders to provide the necessary control over reactant residence time and temperature (107,108). The other route involves adding a third component, interfacially active, block or graft copolymer "compatibilizer" to the immiscible binary mixture (109). Numerous studies in the literature have shown that the incorporation of suitably chosen block copolymers can improve interfacial adhesion (93), provide a measure of stability against gross segregation and permit a finer dispersion during melt processing (110-112), and improve blend mechanical properties (113-115). Regardless of the preparatory route employed, the blocks and grafts must be chosen so that a portion of the compatibilizing ingredient is miscible in each of the primary components which define the interface. This choice can require, once again, knowledge of the enthalpic interactions responsible for polymer-polymer miscibility.

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OXAZOLINE REACTIVE POLYMERS

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OXAZOLINE REACTIVE POLYMERS

Blends of polymers have focused on those polymer combinations which have adequate physical compatibility. However, if functional groups are incorporated into polymers, they can facilitate interaction of those polymers and allow otherwise incompatible polymers to form good blends.

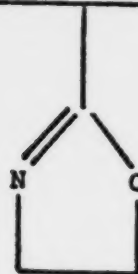
Oxazoline functionalized polymers provide a reactive grafting site which can be used to bond dissimilar polymers. Such covalent bonding overcomes the tendency of those polymers to form poor blends due to interfacial weakness. The oxazoline functionality was chosen to demonstrate compatibility through polymer grafting because it is uniquely suited for polymer blending operations. Under normal melt blending conditions an oxazoline reactive polymer will graft to another coreactive polymer rapidly, with a controllable graft level, and with an absence of by-products to produce a stable polymer blend, typically marrying the physical characteristics of dissimilar polymers.

Examples of the utility of this polymer grafting will be demonstrated not only for producing unique polymer alloys, but also as a way to chemically bond coextruded films, to react additives into polymers, and to bond with other materials in making composite products.

The plastics compounder continually seeks new polymer combinations and blends to extend the suitability of basic polymers for plastic applications. In its simplest form, a compounder physically mixes polymers and additives relying on the rheology of the system or natural polymer compatibility to hold the blend together and achieve the desired property improvement. Recent advances in polymer blending technology have come from controlled rheology of polymer pairs, the use of miscible polymers (polyphenylene oxide/polystyrene), or the structuring of interpenetrating polymer networks (IPN). All of these systems are limited to specific polymer combinations which have an inherent physical affinity for each other.

The Dow Chemical Company has lifted the science of polymer blends to a higher level of sophistication with its recent introduction of reactive polymers. These polymers are differentiated from other reactive polymers such as epoxies or silane coupling systems which generate thermoset products. Dow's reactive polymers are optimized to permit controlled grafting of polymer systems. This controlled grafting allows otherwise incompatible polymer combinations to be

Polymer Backbone



Oxazoline Ring

Fig. 1. Oxazoline reactive polymer.

REACTIVE POLYSTYRENE (RPS)

Typical Properties

Appearance	Clear, colorless pellets
Molecular Weight	200,000
Functionality	1% oxazoline
Melt Flow Rate	7 g/10 min
Yield Tensile Strength	5300 lb/in ²
Tensile Modulus	420,000 lb/in ²
Ultimate Elongation	2%
Vicat Softening Point	225°F
Izod Impact Strength	.2 ft lb/in of notch
Specific Gravity	1.04

TABLE I

"compatibilized" while still retaining their thermoplastic character. Such a system can be comparable to products like ABS, high impact polystyrene, or grafted polyolefin-rubber combinations which are synthesized by basic polymer producers. What the Dow reactive polymer system does, is extend polymer grafting capability to the plastic compounder because of its novel but straightforward chemistry. And it expands polymer blending to unique combinations which a compounder can target for specific application requirements.

The key which unlocks this capability is the functional oxazoline group incorporated into Dow's reactive polymers (see Figure 1).

This oxazoline group readily reacts with a number of other functional co-reactive groups to chemically bond the two products together.

REACTIVE POLYSTYRENE

The initial reactive polymer which Dow is introducing to the industry is a reactive polystyrene designated by Dow as developmental polymer XUS-40056.01. This product is a general purpose polystyrene which incorporates approximately 1% of the oxazoline functionality into the polymer backbone (Table 1).

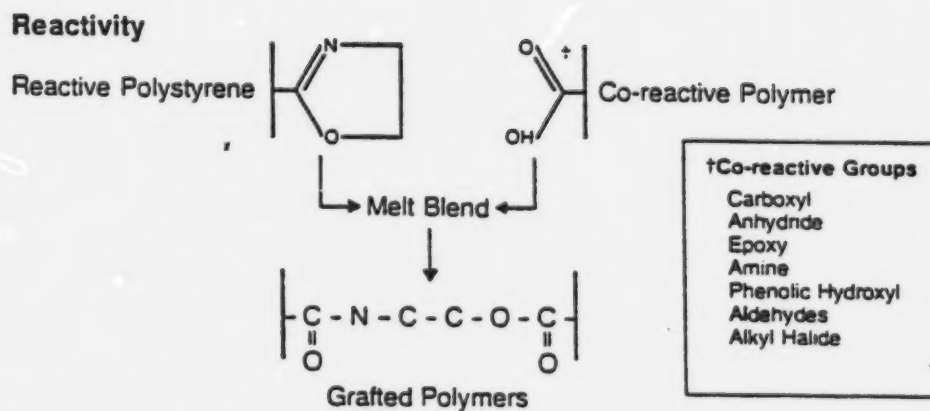


Fig. 2. Oxazoline Reactivity

Reactive polystyrene (RPS) may also be followed to the marketplace by other reactive styrenics, such as high impact polystyrene, ABS, or SAN polymers functionalized with the oxazoline group. RPS itself is a general purpose polystyrene and has been rapidly introduced as a market development product to introduce the concept of reactive polymers to the industry. Ultimate development of additional reactive styrenics will be dependent upon the needs of the marketplace. Indeed, other classes of polymers such as latexes and acrylics have also been fabricated which exhibit the same reactive characteristics as the RPS. Reactive styrene/butadiene latexes are being developed by Dow for use in coating systems and adhesives to take advantage of the chemical bonding capability of the oxazoline functionality. Similarly, reactive acrylic polymers are being developed in application areas where an acrylic base is preferred to the styrenic because of its superior weatherability.

CHEMICAL BONDING

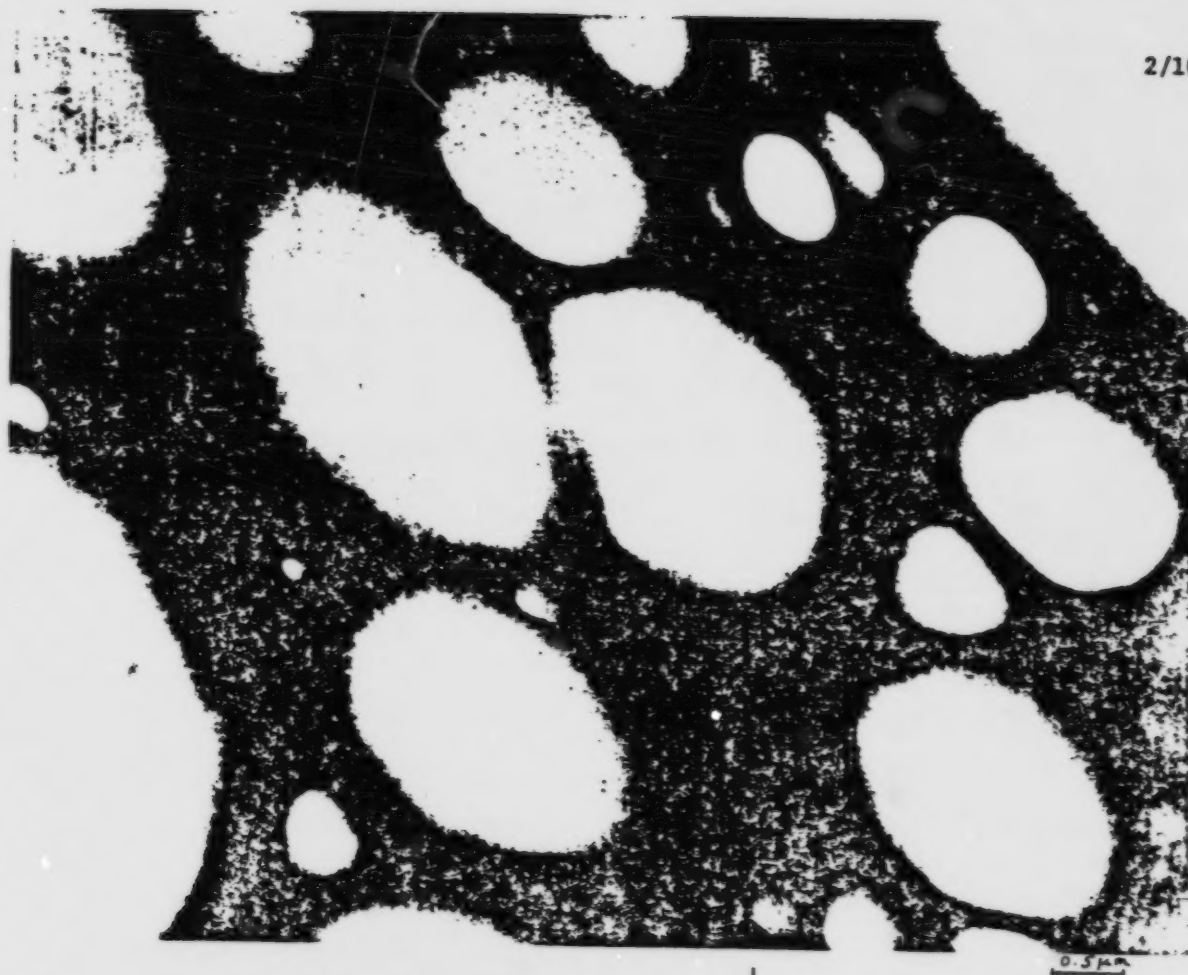
RPS, with its oxazoline functionality, offers only one-half of the bonding equation. It must be combined with another polymer or material that can react with the oxazoline group (Figure 2). A common co-reactive group is an acid functionalized polymer such as Dow's PRIMACOR® 3440 or 1430 (polyethylene acrylic acid). Other modified polyolefins such as DuPont's ionomers (Surlyn® 9450) or Reichhold's polypropylene (Polybond®1001) have been reactively grafted with RPS. When RPS is combined with these co-reactive

polymers, the oxazoline ring opens and stable chemical bonds are formed between the polymers. To activate this reaction it is only necessary to melt mix the RPS and the co-reactive material. The bonding occurs very rapidly (approximately 1 min.) at melt mixing temperatures of 400°F and without any reaction by product, such as gas or water. In fact, the key to this reactive polymer bonding is adequate mixing of the polymers to allow the reactive oxazoline and the co-reactive groups to physically contact each other. For this reason, optimum polymer bonding occurs when the polymers have adequate melt flow properties (normally >2 melt index).

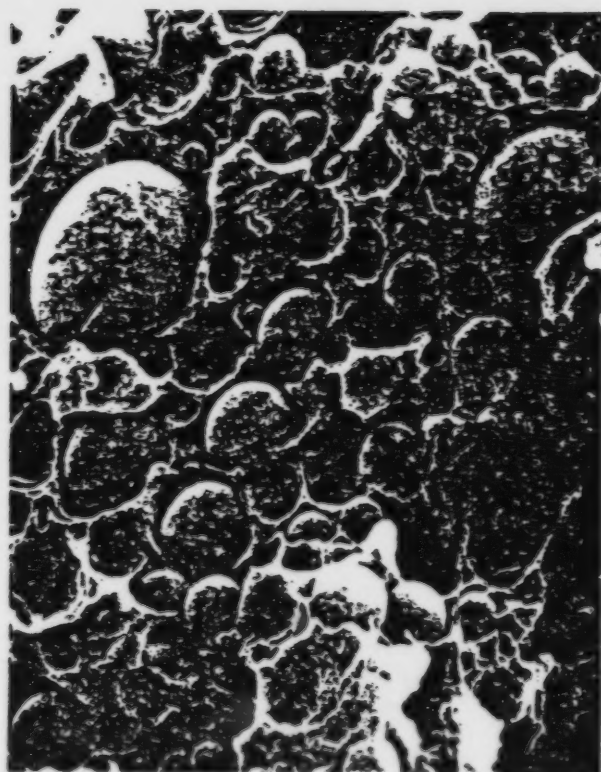
While good polymer mixing and adequate melt flow are important to reactive polymer blending it is also desirable to alloy with RPS a polymer with comparable viscosity so that moderate shear can facilitate a homogeneous blend. In addition, the polymer must have an adequate level of co-reactive functionality (generally 1% or more) so that the oxazoline level on RPS limits the amount of grafting which occurs. Also, since two distinct polymer phases result from the incompatible but grafted polymer alloys, the proportion of RPS in the alloy would normally be maintained at less than 50%. Such an alloy will result in RPS as the discontinuous phase and acting as a styrenic reinforcement for the continuous phase.

It has been found that extrusion equipment is ideal for the reactive processing described here. Because mixing is important for best reaction, a twin screw extruder with compounding sections is the preferred unit for polymer bonding. However, successful reactive blends have been produced on a single screw extruder if the materials are processed with a second pass.

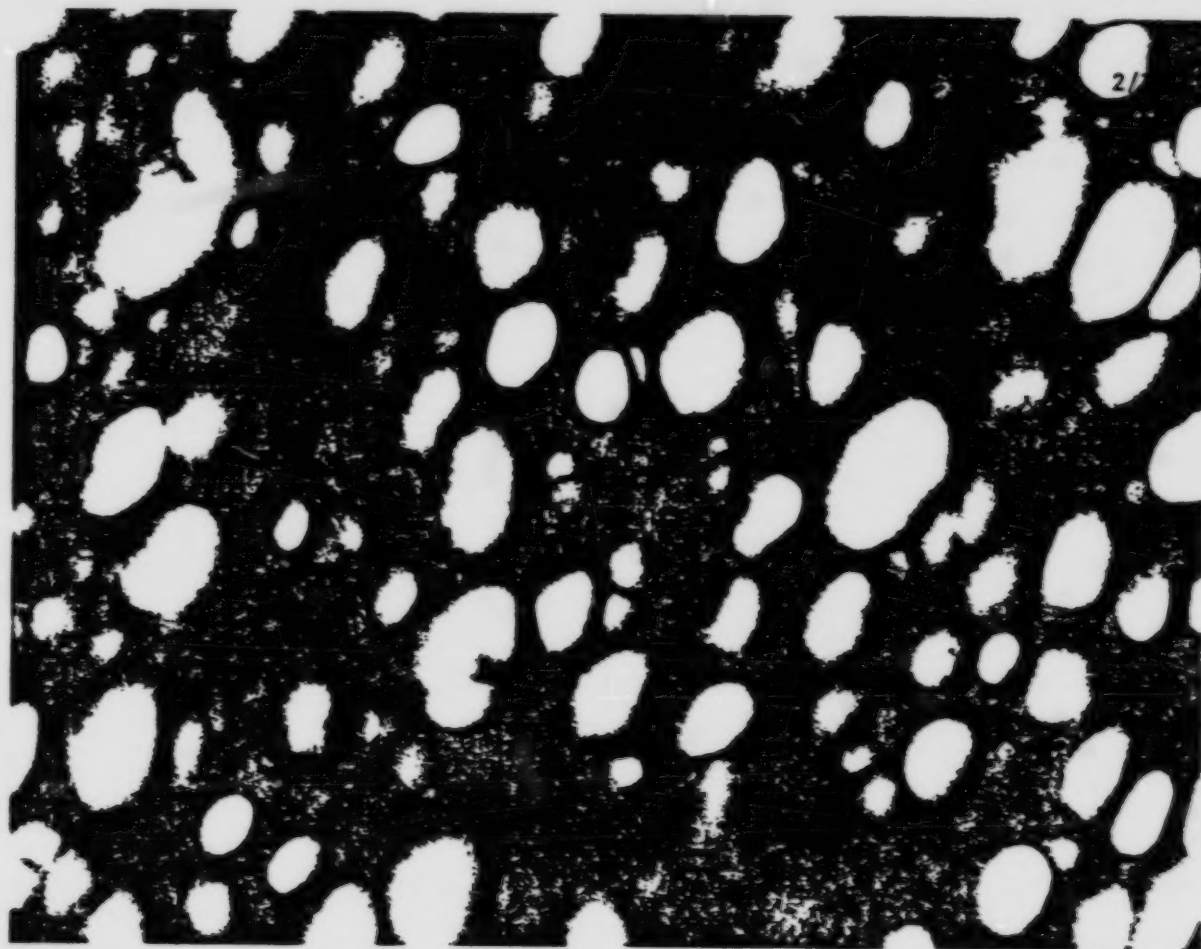
It is evident that in spite of the polymer grafting which occurs, the reactive blend still retains its thermoplastic character. In the reactive blending process it is important to achieve an adequate level of grafting between the polymers so as to compatibilize them, without excessive bonding that could result in a quasi-thermoset blend. This grafting level is controlled by the chosen level of 1% oxazoline in the reactive polymer which provides about 20 reactive sites on each polystyrene chain. A good method for monitoring the level of grafting which occurs is to check the melt flow of the resulting polymer alloy. Compared to a non-reactive control, the reactive polymer blend will exhibit a reduction in melt flow as the level of grafting increases. Reactive polymers with a melt index of 10 will typically result in a blend melt index less than 5, depending on the level of grafting which occurs. If the graft level is excessive, it can easily be reduced by extending either the RPS or the co-reactive polymer with non-reactive but compatible polymers. In this way a compounder can combine as many as four polymers (2 reactive, 2 non-reactive) to achieve an optimized balance of blend properties.



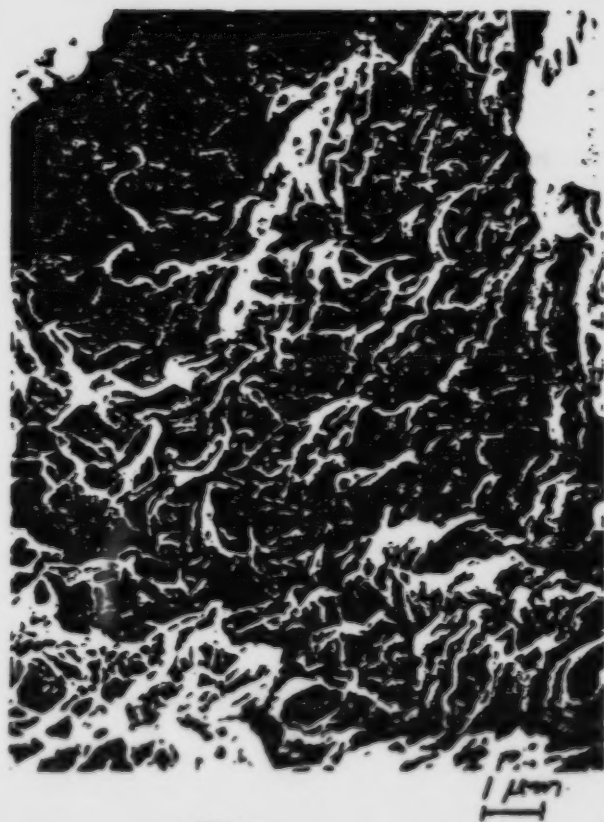
↓
Fig. 3A. Polystyrene/Polyethylene incompatible blend (28,500 X, thin section).



→ Fig. 3B. Polystyrene/Polyethylene incompatible blend (5,000 X, fracture surface).



↓
 Fig. 4A. Reactive polystyrene/polyethylene alloy
 (28,500 X, thin section).



→ Fig. 4B. Reactive polystyrene/polyethylene alloy
 (5,000 X, fracture surface).

Depending upon the reactive/co-reactive polymer blend it may be desirable to enhance the reactivity of the blend. Certain co-reactive groups (epoxy, hydroxyl) need to be catalyzed to react with the oxazoline. Even with the more active co-reactive groups, one can expect only about 50% of the theoretical maximum bonds to be formed. Addition of 0.1% of a catalyst, such as zinc chloride will enhance the reactivity of such blends.

COMPATIBILIZE BLENDS

Much work has been done in recent years on blends and alloys of polymers. Most of this work has dealt with polymer blends that are physically compatible or utilize a third component compatibilizer. Regardless, there are strict limitations on the type of polymers which can be blended while retaining their good physical properties. When incompatible polymers are combined, a heterogeneous blend is obtained (Figure 3) which exhibits poor physical properties. However, when these same polymers are combined by reactive oxazoline grafting, the resultant blend is a tough, homogeneous polymer with good physical properties. The photo-micrograph (Figure 4) is of a 50% blend of polyethylene acrylic acid and 50% RPS. The white particles are RPS dispersed in the polyethylene continuous phase. Notice that the reactive polymer blend disperses the polystyrene uniformly and in very small particle phases compared to the control. Also, the interface of the RPS phase is grafted into the polyethylene to reinforce the

TABLE II
PROPERTIES OF POLYMERS ALLOYED WITH RPS

	<u>POLYOLEFIN</u>	<u>POLYSTYRENE</u>	<u>ALLOY</u>
Heat distortion	Good/Fair	Fair	Good/Fair
Distortion under load	Poor	Good	Good
Tensile strength	Fair	Good	Good
Modulus	Poor	Good	Good
Elongation	Excellent	Poor	Good
Impact strength	Good	Poor	Good
Environmental stress crack resistance	Good	Poor	Good
Cost	Good	Good	Good
Processability	Poor	Good	Good

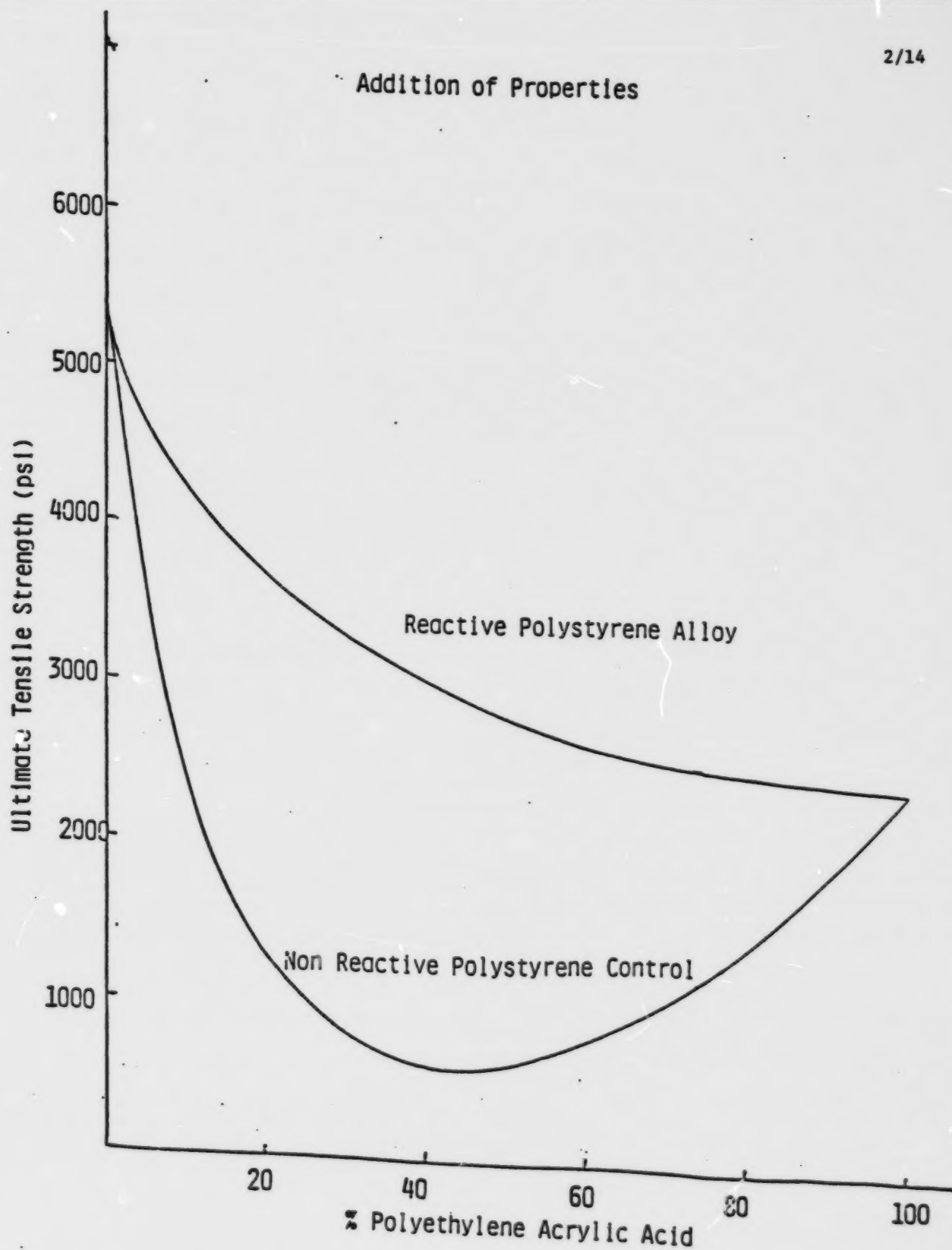


Fig. 5. Polymer blend property profile.

structure.

The control blend results in a dramatic drop in impact, tensile, and elongation properties, while the reactive blend yields a marriage of properties. In effect, reactive polymer processing removes the limitations of otherwise incompatible polymer combinations. Through oxazoline grafting, polystyrene alloys have been achieved with co-reactive functionalized:

Polyethylenes

Polypropylenes

Rubbers

Polyesters

Epoxies

Acrylics

Nylons

A continuum of properties is achieved ranging from the styrenic properties of RPS to those of the co-reactive polymer (Figure 5). A plastics compounder now has an additional tool to overcome certain polymer deficiencies by combining polymers which previously could not be accomplished (Table II). In effect, the plastics compounder can now produce his own unique grafted polymers using his extruder as a reactor and giving him polymer design capabilities that were previously limited to the thermoplastic polymer producers. Even polymer producers are attracted to the concept of developing grafted polymer blends without having to

TABLE III

HDPE/RPS ALLOY WITH ABS PROPERTIES (COMPRESSION MOLDED VALUES)

	<u>RPS</u>	<u>HDPE*</u>	<u>ALLOY 60% HDPE* 40% RPS</u>	<u>ABS 9030</u>
TENSILE YIELD (PSI)	5,300	2,700	4,100	4,500
TENSILE MODULUS (PSI)	420,000	160,000	290,000	240,000
% ELONGATION (BREAK)	2	900	60	32
NOTCHED IOD IMPACT (FT-LB/IN)	.2	2	4	6
VICAT HEAT DIST (°F)	225	260	243	226
DTUL (264 PSI) (°F)	183	107	185	205
MELT FLOW (G/10 MIN)	7	6	3	2.7
SPECIFIC GRAVITY	1.04	.96	.98	1.05
ESCR (2500 PSI)			700	300
(FREON) ¹ (MIN)				

*FUNCTIONALIZED WITH ANHYDRIDE

¹REGISTERED TRADEMARK OF DUPONT DE NEMOURS AND COMPANY, INCORPORATED

TABLE IV
RPS-HDPE VS. ABS
ADVANTAGES

ELONGATION
VICAT HEAT DISTORTION
ENVIRONMENTAL STRESS CRACK
CHEMICAL RESISTANCE
WEATHERABILITY
LOW SPECIFIC GRAVITY
WHITENESS
LOW TEMPERATURE PROPERTIES
WATER VAPOR BARRIER
FILLER ACCEPTANCE

synthesize polymer grafting processes. An added attraction is the minimum in capital investment required to produce a new line of thermoplastic products.

HDPE/RPS WITH ABS PROPERTIES

When considered alone, neither high density polyethylene nor general purpose polystyrene would be thought of for engineering thermoplastic properties, since both polymers have property deficiencies. However, when RPS is reactively grafted to a functionalized HDPE the resultant alloy possesses a balance of properties similar to a high heat ABS (Table III). It is possible to upgrade the utility of commodity polymers like polystyrene and polyethylene, retain their desirable properties, and in some cases (impact resistance) obtain a synergistic effect through reactive grafting. By grafting RPS into the HDPE, ABS properties are obtained while retaining some of the advantages of HDPE (Table IV).

MANY USES FOR OXAZOLINE "HANDLES"

Although producing unique polymer alloys is certainly a natural application of oxazoline reactive polymers, additional utility is limited only by the imagination of the plastics compounder or fabricator. Consider that in the general sense RPS has oxazoline "handles" that are available to grab onto another product containing a co-reactive group.

CO-EXTRUSIONS

Normally when polystyrene film is coextruded with a polyolefin there is little adhesion between the different polymers. Even if a tie coat adhesive is applied between the layers there can be delamination under processing conditions. However, when RPS film is coextruded with a film of co-reactive polyolefin, the two films can be chemically fused so as to reinforce properties without using glue layers. In fact, the RPS could be thought of as the reactive thermoplastic glue for composite structures.

REACTIVE PLASTIC SUBSTRATES

Reactive polymers can be thermally processed without activating the oxazoline functionality as long as no co-reactive material is present. Thus, one can produce a film, sheet or molded plastic part with RPS and still have oxazoline reactivity available on the surface of those products. This latent reactivity has subsequently been used to apply a coating or paint (with co-reactive groups) and chemically bond it to the RPS substrate. To evaluate this concept, a sheet of RPS was coated with a carboxylated latex, oven dried and compared to a control non reactive polystyrene sheet. When the latex coated control was exposed to a wet environment it quickly lost adhesion. The RPS substrate with the same carboxylated latex maintained excellent adhesion even after exposure to boiling water for 96 hours.

COATINGS

Conversely, a coating system can be produced using oxazoline functionalized polymers that will chemically bond to a co-reactive surface during the drying process. This yields a coating with superior adhesion and excellent solvent resistance. RPS is useful for solvent based coatings while reactive latexes can be used in water based systems. RPS has also been solubilized in liquid epoxy systems for controlled curing of a styrenic/epoxy coating. Possible utility in reactive adhesives remains to be investigated.

REACTIVE ADDITIVES

When additives are incorporated into thermoplastics they act as inert fillers which can detract from the desired polymer properties. With RPS, the compounder now has the capability to react additives like flame retardants, antioxidants, plasticizers, fiberglass, etc. into the polymer backbone. In effect, such additives can be coupled right into the reactive polymer without causing the detrimental effects to the polymer which are often seen.

To demonstrate, a phenolic flame retardant added to polystyrene at a level of 12% reduced its heat distortion temperature by 27°F. The same product reactively grafted to RPS resulted in only a 7°F decrease.

THERMOSETS

The oxazoline level of RPS has been optimized so that the thermoplastic character of polymer blends are retained throughout the grafting process. However, it is possible to incorporate higher oxazoline levels in reactive polymers so that during processing the thermoplastic polymers can be converted to quasi-thermoset materials. This reactivity was demonstrated to be useful in a powder coating polymer system. There, a highly oxazoline functionalized polymer and co-reactive component were applied to a metal panel as a thermoplastic powder. As the polymer is melted, oxazoline reactivity precedes and produces a highly cross-linked thermoset coating. Such characteristics can be useful in areas such as hot melt adhesives, RIM systems, or other applications where higher heat performance properties are desirable.

OXAZOLINE - THE LINK TO NOVEL POLYMERS

Oxazoline functionality on a polymer provides a bonding site to graft those polymeric properties onto another polymer or material. No longer does one have to rely on polymer compatibility to produce polymer blends with reinforcing properties. Oxazoline reactivity is ideally suited to the plastics compounder using his extruder as a reactor -- rapid, thermoplastic, by-product free, and thermally stable. Reactive polystyrene is the first of what may be a new family of reactive polymers that will extend the limits of achieving unique polymer combinations.

NMR Studies of Ionomers 6. Polyurethane - Polyphosphonate Blends

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ABSTRACT

Blending of a poly(ether urethane) with a polyphosphonate obtained by phase transfer catalysed polycondensation of 4,4'-biphenol and chloromethylphosphonic dichloride generates a phase-separated material. One phase contains the soft segment of the polyurethane which has been excluded from a high-T_g phase containing ionic species formed mainly by proton transfer and elimination reactions between the hard segment of the polyurethane and the polyphosphonate. Two glass transitions appear in the blend : one close to the T_g of the polyphosphonate and one belonging to the excluded soft segment of the polyurethane. The low temperature T_g decreases with the increasing content of the polyphosphonate, whereas the high temperature transition increases slightly, indicating an increasing purity of the soft segment and the presence of ionic interactions in the hard segment. The presence of ionic interactions is confirmed by NMR analysis of the blend. Comparison of the spectra of the blends with those of the pure components, along with two-dimensional experiments, indicate a reaction involving the chloromethyl groups of the polyphosphonate and the nitrogens of the polyurethane.

INTRODUCTION

Segmented polyurethane containing polyether or polyester groups as soft segments are receiving considerable attention, partly because of their extensive industrial applications. The presence of both soft and hard (urethane moieties) segments can, in some cases, generate partial or complete phase separation within the material, which can result in very favorable mechanical properties. The most attractive feature of this behavior is the possibility of controlling the properties by modifying the chemical structure of the polyurethane. For example, phase separation occurs in these systems if the molecular weight of the soft segment exceeds 830 (1,2).

Another way to modify the mechanical properties of a polyurethane is by mixing it with various other polymers. In this laboratory, polyurethanes were blended with a series of polymers that are able to generate ionic species. For example, mixing a one-phase poly(ester-urethane) with poly(styrene-co-styrene sulfonic acid) (poly(S-co-SSA)) produces a phase-separated material with two glass transitions. The lower T_g decreases with increasing styrene content, while the higher T_g increases up to the value of the T_g of poly(S-co-SSA) (3). This phenomenon can be explained on the basis of a proton transfer from the SSA group (4) to different nitrogen atoms present on the polyurethane chain (5,6). The proton carries a positive charge which is located now on the polyurethane chain, while poly(S-co-SSA) contains negative pendant ions. The Coulombic interactions between these charged chains render poly(S-co-SSA) miscible with the hard segment of

the polyurethane, excluding the soft segment as a separate phase, leading to a phase-separated material.

As part of a continuing investigation, polyurethanes have been blended with various polymers (7,8) in an effort to produce materials with a wide range of mechanical properties. This paper presents the results of blending of a poly(ether-urethane) with a polyphosphonate obtained by phase transfer catalysed polycondensation of 4,4'-biphenol with chloromethylphosphonic dichloride. Aromatic polyphosphonates have been recently synthesized and tested for use as possible high-performance plastics (9). Their glass transition temperature can be very high if appropriate aromatic diols are used in the synthesis. Also, the phase transfer catalysed procedure allows for better thermal stability of the polymer, by eliminating labile end-groups (10,11). The presence of chloromethyl side groups has been shown to improve compatibility with a series of commercial polymers (10). Therefore, an aromatic polyphosphonate containing chloromethyl side groups has been chosen to form blends with a poly(ether-urethane).

NMR spectroscopy proved to be extremely useful in investigating the mechanism of interaction in polyurethane blends (6,8). Model studies and two-dimensional J-correlated homonuclear spectra revealed that the acidic proton of poly(S-co-SSA) is transferred to several sites. In order of preference, these are the secondary structures, the urethane nitrogen and the tertiary nitrogen of the N-methyl diethanolamine (MDEA) chain extender of a poly(ester-urethane) (6). Mixtures of the same poly(ester-urethane) with chlorinated polyisobutylene were the subject of a

previous study. NMR spectroscopy, in combination with other methods, revealed the existence of two reactions. The main one was a dehydrochlorination process, with the resulting HCl reacting with the polyurethane nitrogens, generating ionic groups. The second reaction was an interaction between the polyurethane nitrogens and the chloromethyl groups of the chlorinated polyisobutylene side chains, which also generated positive and negative charges (8). In this paper, NMR spectroscopy is also utilized in combination with dynamic mechanical analysis to investigate the mechanism of interaction in a poly(ether-urethane) - polyphosphonate blend.

EXPERIMENTAL

Synthesis of polyurethane

The poly(ether-urethane) was prepared by a two-step condensation reaction (3). Polyoxytetramethylene diol (PTMO, average MW = 930) was dried under vacuum at 60° C for 5 hours. 4,4'-Methylene bis(phenyl isocyanate) (MDI) was purified by filtration of the liquid at 70° C. N-Methyldiethanolamine (MDEA), stannous octoate catalyst and anhydrous N,N'-dimethylformamide (DMF) were used as received. The prepolymer was prepared as follows: MDI was dissolved in DMF at a concentration of about 40% by weight. This solution was added to a solution of DMF, PTMO (40% by weight) and stannous octoate (0.1% by weight).

The synthesis of the urethane prepolymer was carried out at 65° C for 2 hours under vacuum, maintaining a NCO:OH molar ratio of 3:1. The chain extender (MDEA) was added in an appropriate quantity to maintain a NCO:OH ratio of 1:1 and the reaction was

continued for an additional hour. The polyurethane was precipitated with warm water and dried under vacuum at 80° C for two weeks.

Phase Transfer Catalysed Synthesis of the Polyphosphonate

The polycondensation of 4,4'-dihydroxybiphenyl with chloromethylphosphonic dichloride was carried out according to the published method (10). It was performed in an aqueous NaOH - chloroform system using the phase transfer catalyst tetrabutylammonium hydrogen sulphate (TBAH) at -5 - -8° C. The polyphosphonate was soluble in chloroform. After washing with water to a neutral pH, the polymer was precipitated with methanol.

Blending

The polyurethane was dissolved in DMF. The polyphosphonate was also dissolved in DMF, and this solution was added dropwise to the vigorously stirred polyurethane solution. The mixture was stirred for 5 hours and subsequently dried by evaporation of the solvent at progressively higher temperatures (up to 70° C) under vacuum; the blends were then annealed at 120° C for 24 hours.

Sample Preparation for Dynamic Mechanical Studies

The samples used for the torsion pendulum measurement were prepared by compression molding of 1.0 g of the blend. The polymers were heated in the mold to a temperature above 100° C for about one hour at 45 MPa. The sample was removed from the mold after it had cooled to room temperature. Typical dimensions of the specimens were 2.5x6x50 mm.

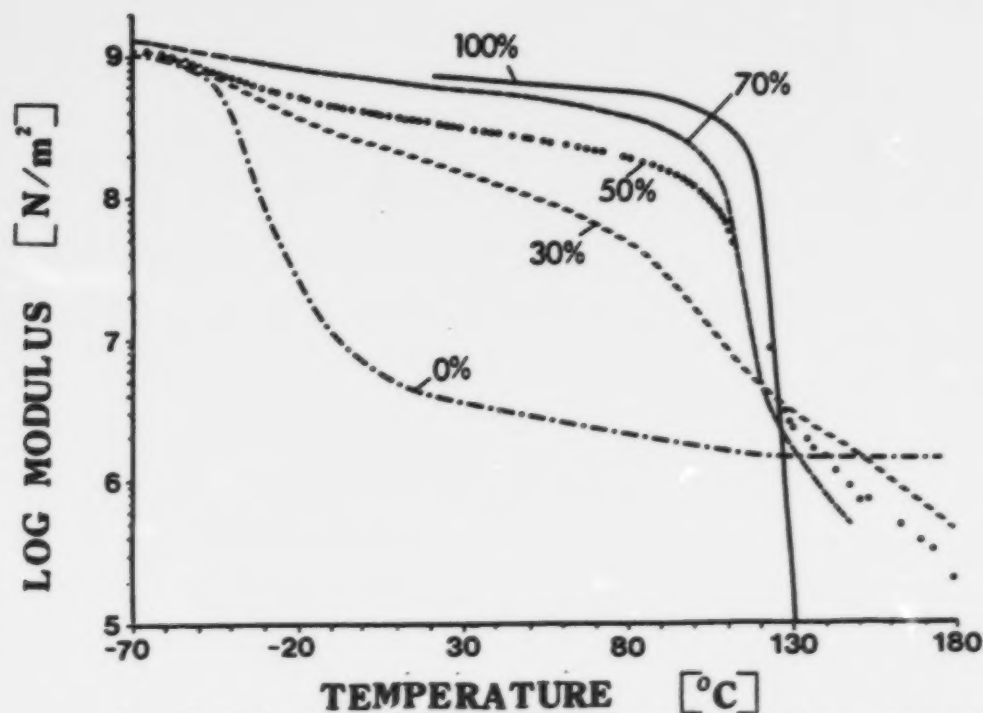
Dynamic Mechanical Studies

Dynamic mechanical studies were performed under dry helium between -10 and $+180^{\circ}\text{C}$ using a computerized torsional pendulum partly described elsewhere (12). The frequencies varied from ca. 4 to 0.1 Hz depending on the temperature. The heating or cooling rates were always less than 1°C/min .

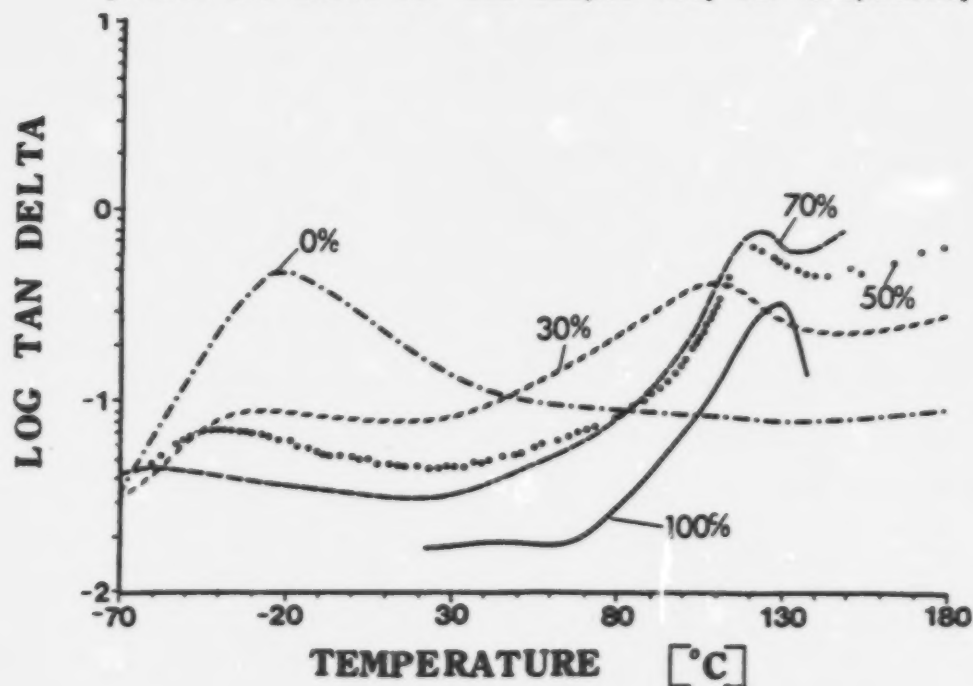
NMR Spectra

Proton, carbon and phosphorus spectra were taken in DMSO-d_6 (100% deuterated, Aldrich) solutions on a Varian XL-300 spectrometer using pulses of 40° and no delay between them. The acquisition time was of ca. 4 seconds, considered long enough to ensure relaxation.

Two-dimensional pulse sequences offered by Varian (13) were used to obtain COSY, NOESY and HETCOR spectra. The COSY spectra (homonuclear correlated) were obtained with a DQF sequence, which provided suppression of the intense signals on the diagonal. The NOESY spectra (through-space dipolar correlated) were obtained with a NOE2D sequence containing a mixing interval which was estimated to be of 0.3 s from T_1 measurements in the analysed samples. Also, an increment in the mixing time was provided by the software and allowed for the J-correlated cross-peaks to be spread while the position of NOE or exchange peaks was maintained. Both DQF and NOE2D sequences were applied to a double spectral window, in order to avoid the presence of quadrature image peaks. This procedure was previously reported by other authors (14). The P-H HETCOR spectra were obtained using the P-H coupling constant measured in the proton spectra (10 Hz).



1. Variation of the shear storage modulus with temperature for blends PU/PPh with varying contents of PPh. The number indicates the weight % of the polyphosphonate in the blend. Experimental points are shown for one sample only for simplicity.



2. Variation of the loss tangent with temperature for blends PU/PPh with varying contents of PPh.

RESULTS AND DISCUSSION

Dynamic mechanical studies

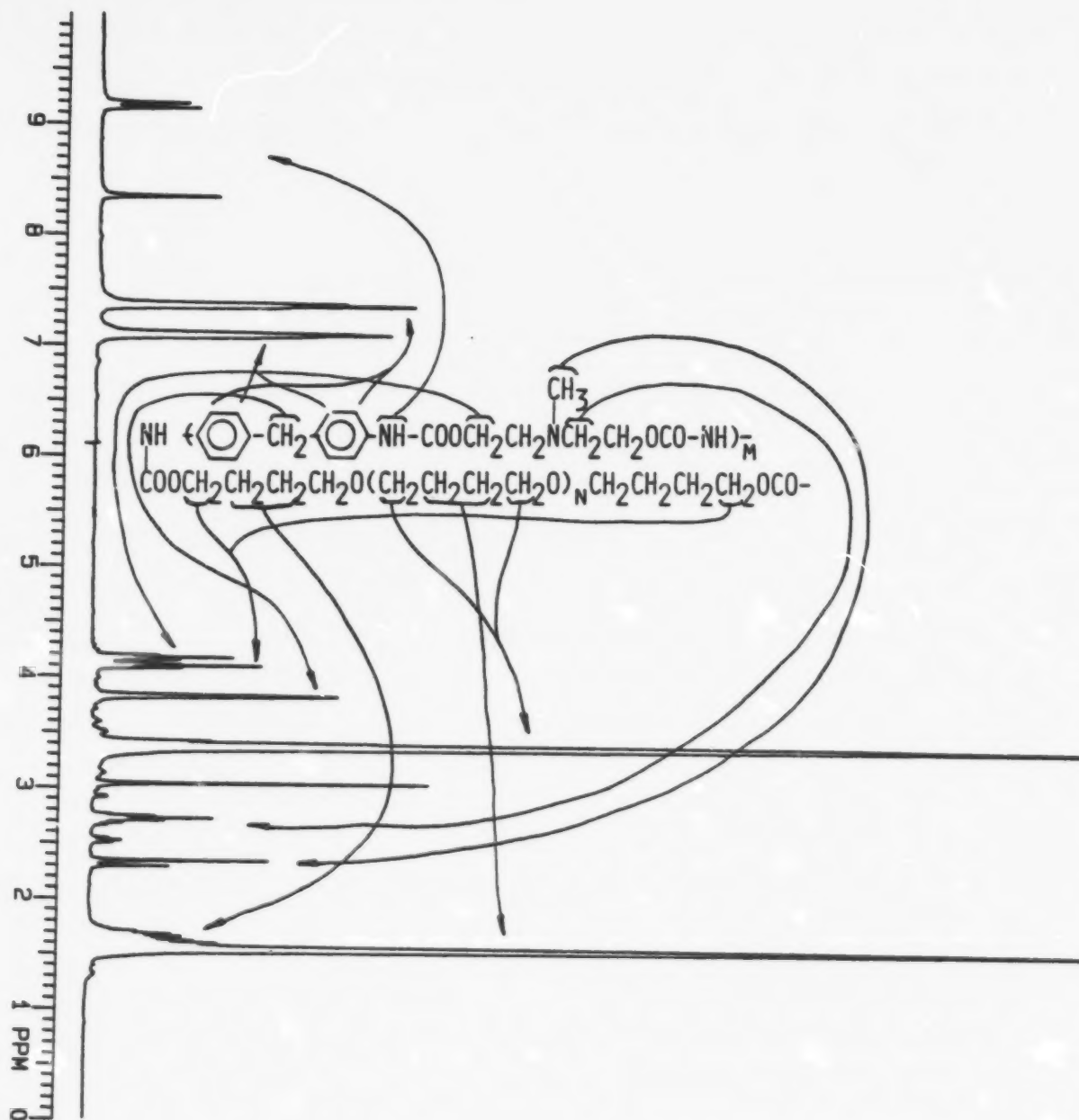
Figure 1 shows a plot of the shear modulus (G') versus temperature for the polyurethane blended with varying amounts of the polyphosphonate. The corresponding loss tangent plots are shown in Figure 2.

Figure 1

Figure 2

The plots for pure polyurethane (0% sample) and pure polyphosphonate (100% sample) show clear evidence of a one-phase system. The 30%, 50% and 70% samples, by contrast, show behavior of two-phase systems that can be seen in a two-step descent in the moduli and in the presence of two peaks in the loss tangent plots. The peak positions for the low temperature glass transition are strongly composition dependent. This suggests that a mixture is indeed formed and that the soft segment is being separated from the hard segment as was previously shown for other systems (3,5). One can also see that the glass transition temperature of the polyphosphonate decreases with increasing polyurethane content, showing that the compatibilization has been achieved between the polyphosphonate and the hard segment of the polyurethane (3).

In view of the miscibility, it is reasonable to expect that some reactions between the chloromethyl group of the polyphosphonate and the amino group on the polyurethane chain may have occurred and that they are sufficient to achieve the observed miscibility in the present system. Possible reactions

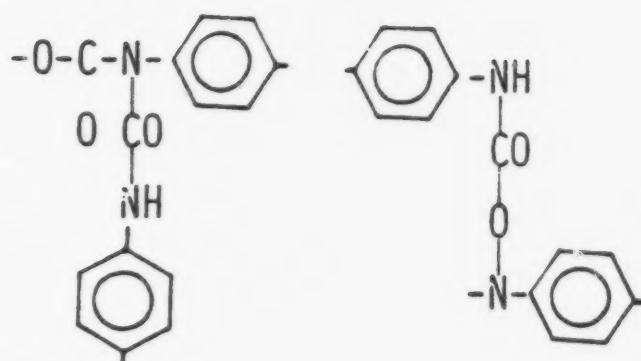


3. ^1H -NMR spectrum of the poly(ether-urethane) in $\text{DMSO}-d_6$.

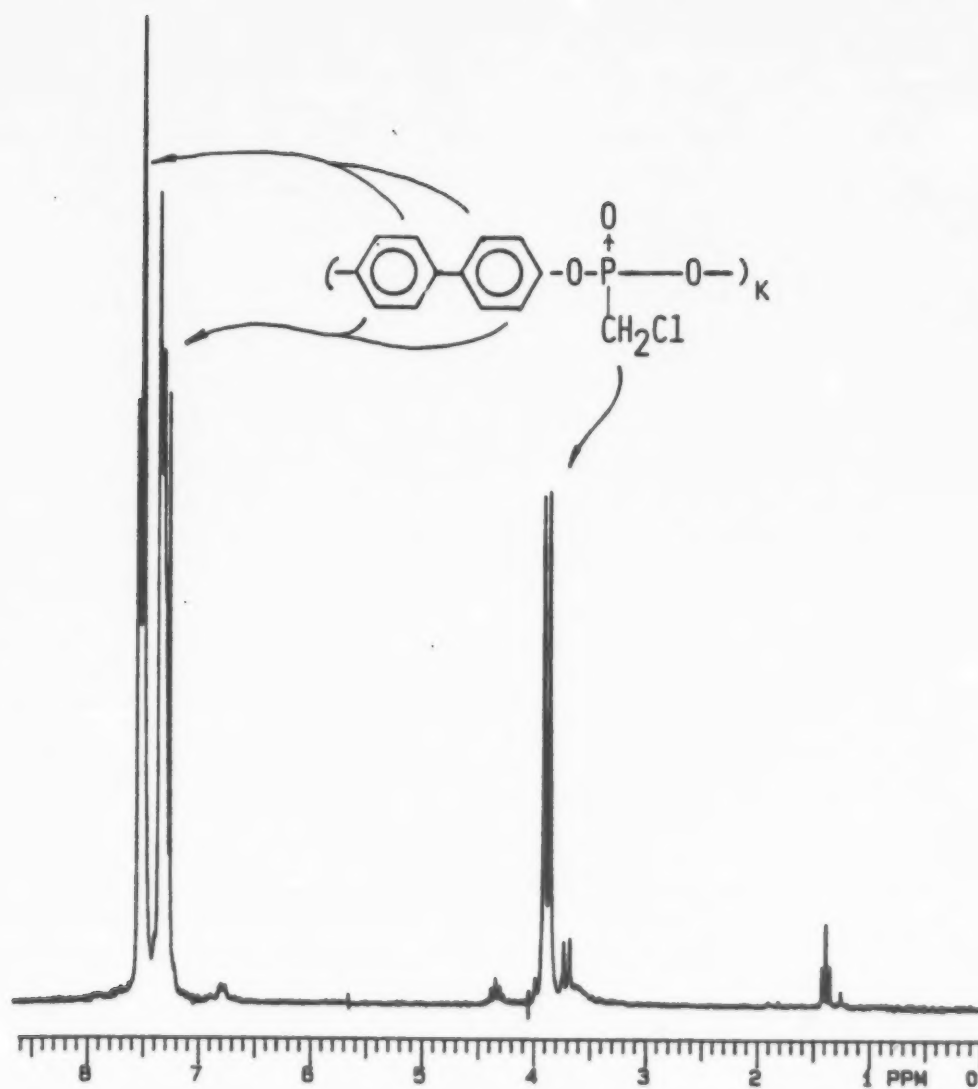
are crosslinking and simultaneous ionization, both of which would raise the T_g of the blend beyond what it would be in the absence of these reactions. Therefore, it is not surprising that the T_g of the blend decreases only slightly with increasing polyurethane content. In the absence of crosslinking and ionization, one would expect a dramatic decrease.

NMR Spectroscopy

Figure 3 presents the ^1H -NMR spectrum of the poly(ether-urethane) registered in DMSO-d_6 . The assignments are given in the figure. The proton spectrum can give information, in this case, also about the average length of the soft segment (poly(ether) molecular weight). This is due to the fact that the chemical shift of a methylene proton differs by more than half a ppm when the methylene is bonded to an ether or an ester oxygen. The terminal units of the soft segment are directly bonded to the urethane carbonyl groups, and the terminal methylene units resonate at 4.10 ppm, whereas the "internal" methylene units give the intense signal at 3.38 ppm. A COSY spectrum shows that even the methylenes 2 and 3 of the tetramethylene unit are sensitive to the link to the urethane hard segment, resonating at 2.68 ppm, whereas the main signal of these groups appears at 2.55 ppm. From the spectrum integral one can calculate an average degree of polymerization of the soft segment to be 10.9, which corresponds to a molecular weight of 785. There are less "impurity" signals in this spectrum as compared with the spectrum of the poly(ester-urethane) (6). The signal at 3.09 ppm is probably due to water traces in the solvent. There are two other small signals at 2.55 and 2.3 ppm that cannot be identified. However, there are three



SCHEME 1



4. ^1H -NMR spectrum of the polyphosphonate in CDCl_3 .

signals in the NH region, when only one would be expected for the proposed structure. As in the previous case (6), the normal polyurethane NH is supposed to resonate at 9.20 ppm, whereas the signals at 9.17 and 8.37 ppm are due to undesired secondary structures (6) (Scheme 1) that were assigned according to the literature data (15). The total area of the NH signals is higher than normal, but the linear polyurethane NH integral is smaller than expected, indicating that a significant part of the hard segments are present as secondary, non-linear structures.

Figure 3

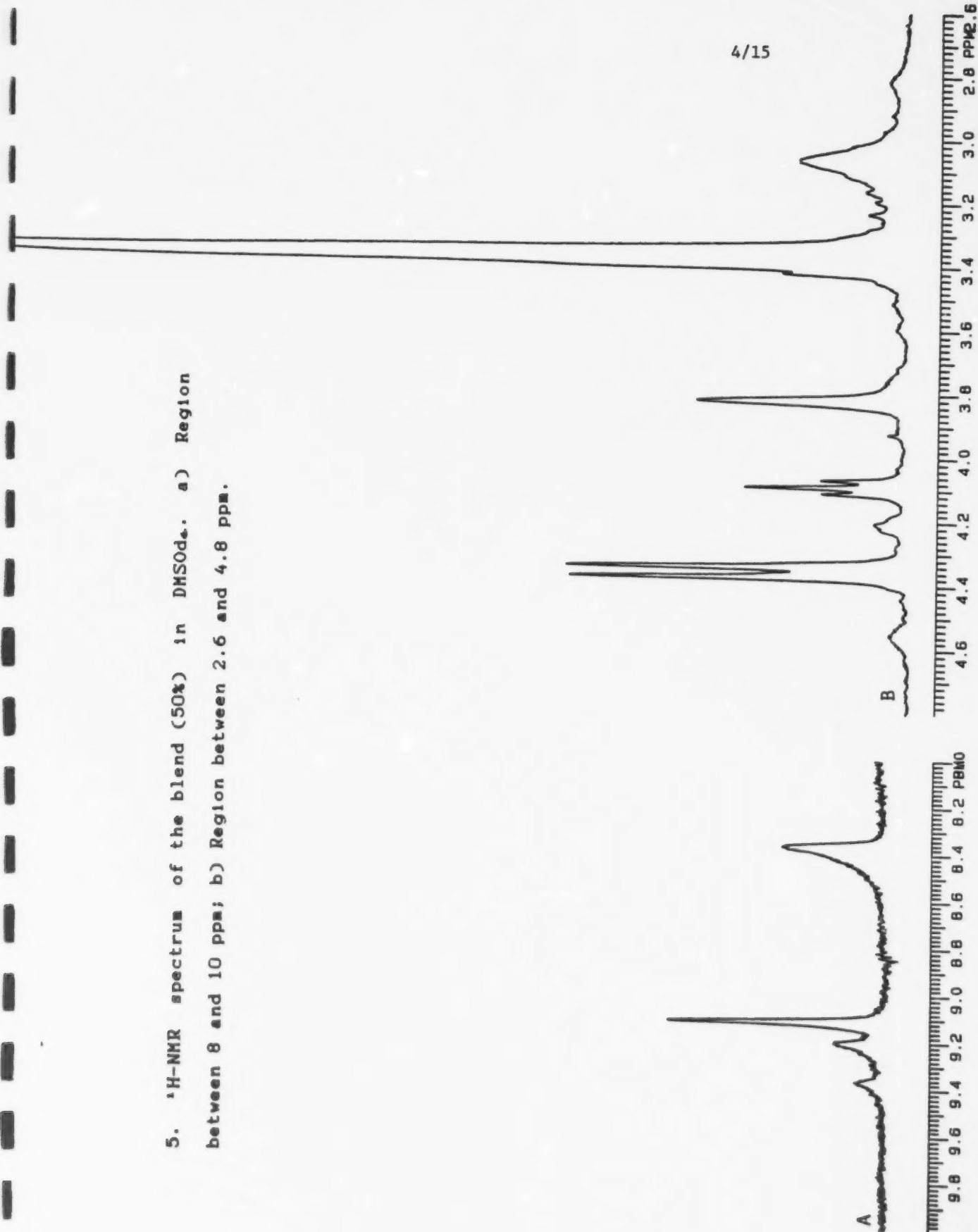
Scheme 1

The ^1H -NMR spectrum of the polyphosphonate in CDCl_3 is presented in Figure 4. The aromatic protons resonate as an AB quartet between 7.2 and 7.6 ppm, and the methylene protons give a doublet at 3.87 ppm (the two-bond P-H coupling constant is 10 Hz). The small doublet at 3.7 ppm appears from the chloromethyl groups belonging to a terminal P-OH group (16). From the integral of the methylene signal one can calculate that there is one terminal P-OH group for every 19 structural units. This amount is significantly higher than expected for a phase catalysed synthesis of the polyphosphonate (10), and suggests incomplete mixing during the synthesis. The ^1H -NMR spectrum in DMSO is essentially identical, with differences only in the chemical shifts.

Figure 4

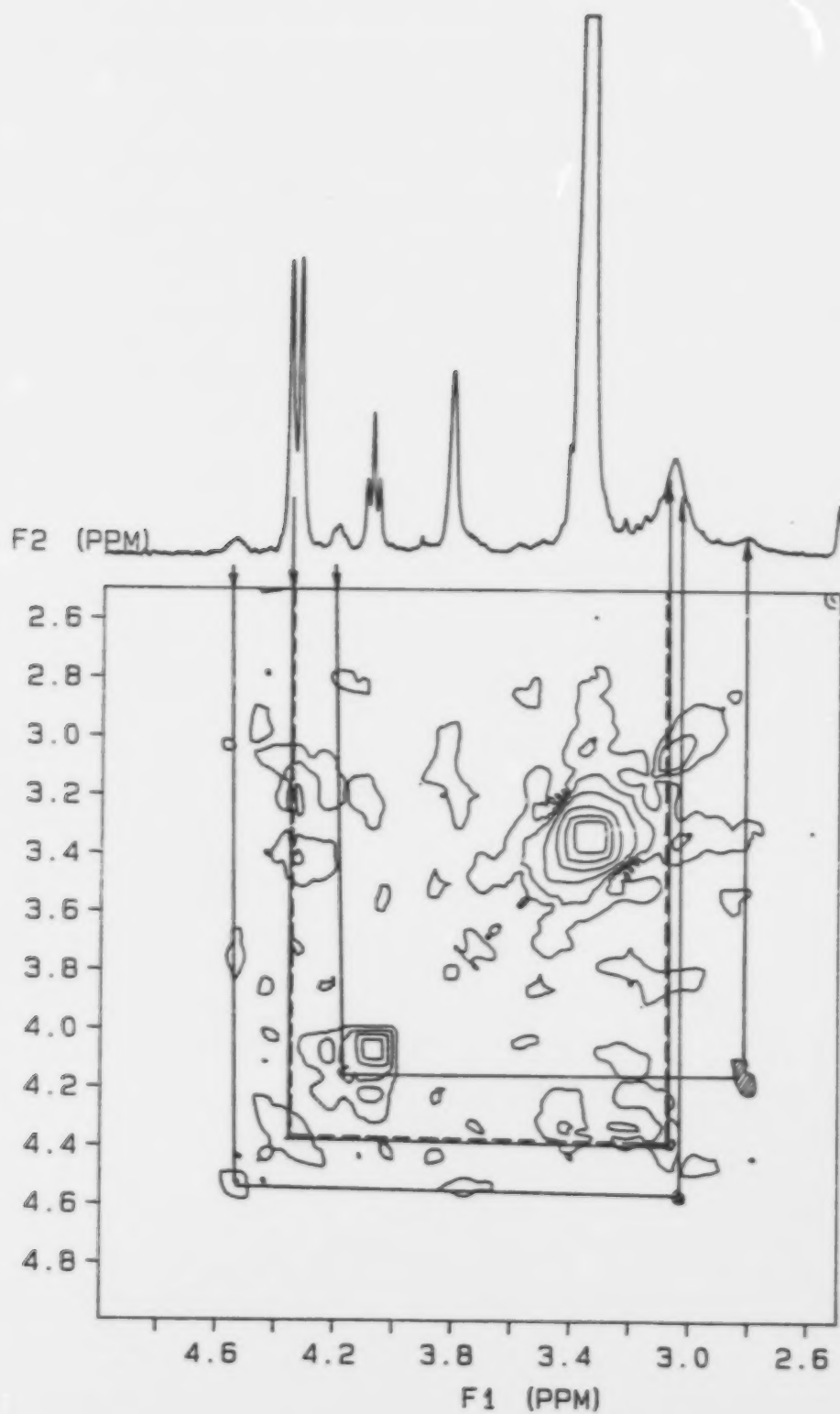
In DMSO, the "inner" aromatic protons resonate at 7.32 ppm and the "outer" ones at 7.7 ppm, whereas the main methylene signal

5. $^1\text{H-NMR}$ spectrum of the blend (50%) in DMSO-d_6 . a) Region between 8 and 10 ppm; b) Region between 2.6 and 4.8 ppm.

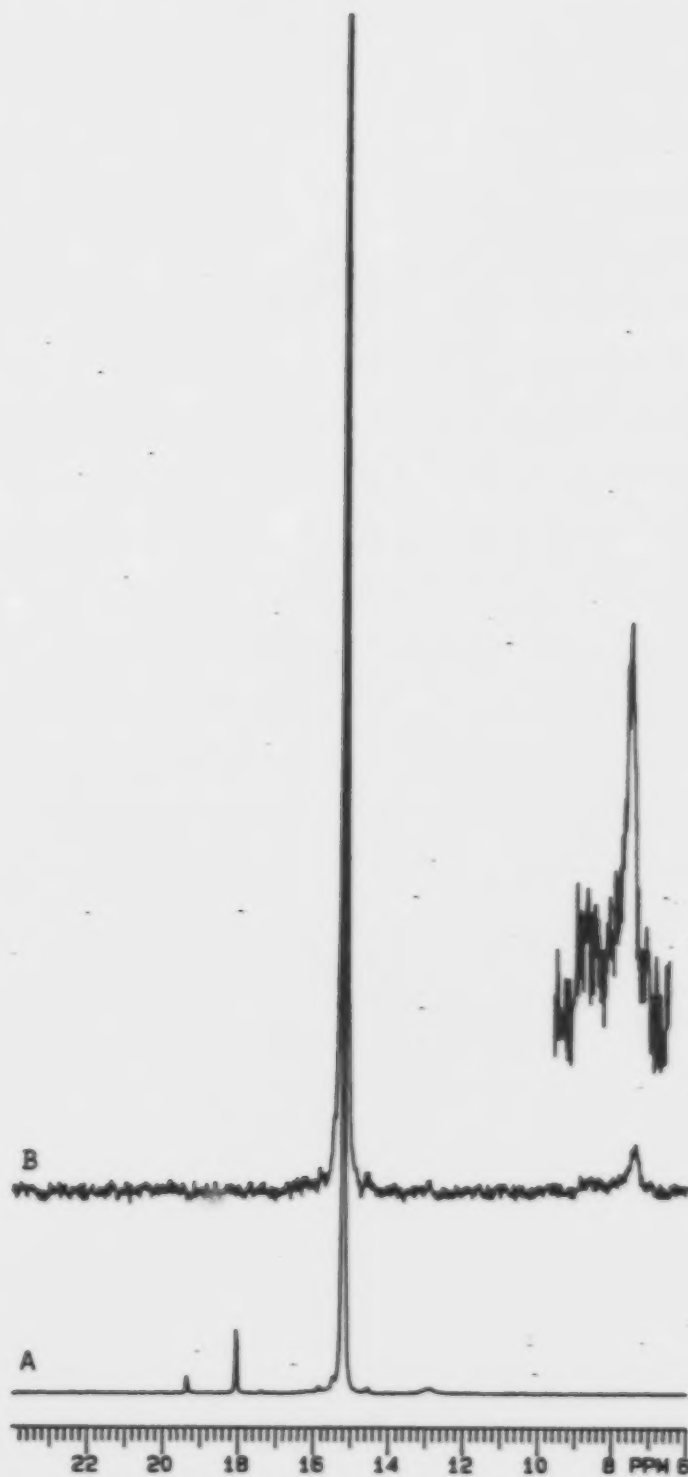


appears at 4.49 ppm and the terminal one at 4.18 ppm. This creates some overlapping with the impurity signal at 4.32 ppm in CDCl_3 (4.23 ppm in DMSO), and this is the reason for presenting here the spectrum in CDCl_3 .

Figure 5 presents those parts of the ^1H -NMR spectrum of the 50% blend which indicate chemical modifications within the blend. For reasons of clarity, the aromatic part, which is simply the sum of the two spectra, and the portion above 2 ppm, which shows no change, are omitted. From the aromatic part of the spectrum one can calculate the molar ratio of the structural units of the two components of the blend. There are two phosphonate units for each MDI residue in the molecule, i. e. two chloromethyl groups for three polyurethane nitrogens. In the NH part of the spectrum, the signal at 9.17 ppm remains unchanged, indicating that this particular secondary structure does not react during the mixing procedure. This particular structure also remained during mixing with poly(S-co-SSA) (6). The other two signals do change, indicating that they were involved in some sort of reaction. In the upper part of the spectrum, the signals that change belong to the MDEA chain extender. As was shown for blends of poly(ester-urethane) with both poly(S-co-SSA) (6) and chlorinated polyisobutylene (8), the signals of about half of the protons belonging to the MDEA residue remain unchanged (at 4.22, 2.84 and 2.43 ppm), whereas the others shift downfield or disappear altogether. This indicates that some of the MDEA residues became positively charged on the nitrogen (6). The signal due to the CH_2O protons of ionic MDEA seem to have shifted to lower field than was observed upon mixing of polyurethane with lightly



6. DQF spectrum of the blend (50%) in DMSO-d₆.



7. ^{31}P -NMR spectra a) of the polyphosphonate and b) of the blend (50%) in DMSO-d_6 .

sulfonated polystyrene (4.58 ppm as compared with 4.46 ppm in the case described earlier (6)).

Figure 5

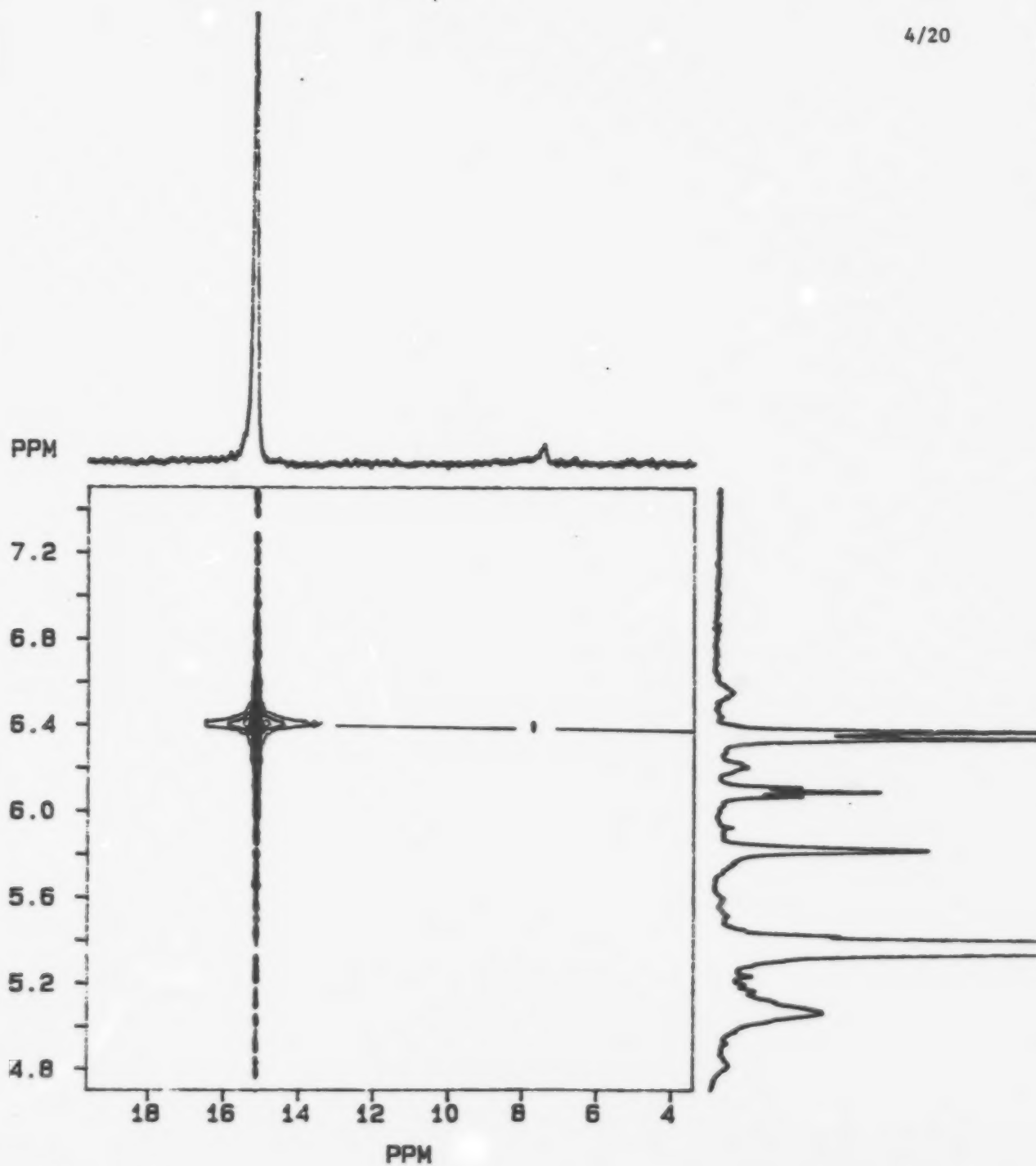
In order to confirm the assignment of this signal, COSY and NOESY spectra were taken. The two-dimensional J-correlated chart for this part of the spectrum is presented in Figure 6. The spectrum does not give clear information, unlike the spectra presented in the previous papers (6,8). This is mainly due to the presence of more intense signals in the area of interest. They produce intense peaks in the two-dimensional chart and when one increases the vertical scale in order to observe cross-peaks corresponding to small signals in the spectrum, a lot of noise appears from the background as well. In figure 6, some correlations that support the theory presented here are underlined, but there is no independent proof that these correlations are indeed real and not artifacts, as most of the cross-peaks are. The NOESY spectra were even less helpful, because the sequence does not provide suppression of intense peaks on the diagonal.

Figure 6

More information can be obtained from the phosphorus and carbon spectra of the blend and components. Figure 7 presents the ^{31}P -NMR spectra of the polyphosphonate (a) and of the blend (b).

Figure 7

One can clearly see the phosphonic end-groups in the polyphosphonate (18.07 ppm) (10), confirming the calculation of 19 structural units in the polyphosphonate for each such end group. Also, there is a very small signal at 19.35 ppm which



8. HETCOR for the phosphorus-proton links in the blend (50%) dissolved in DMSO.

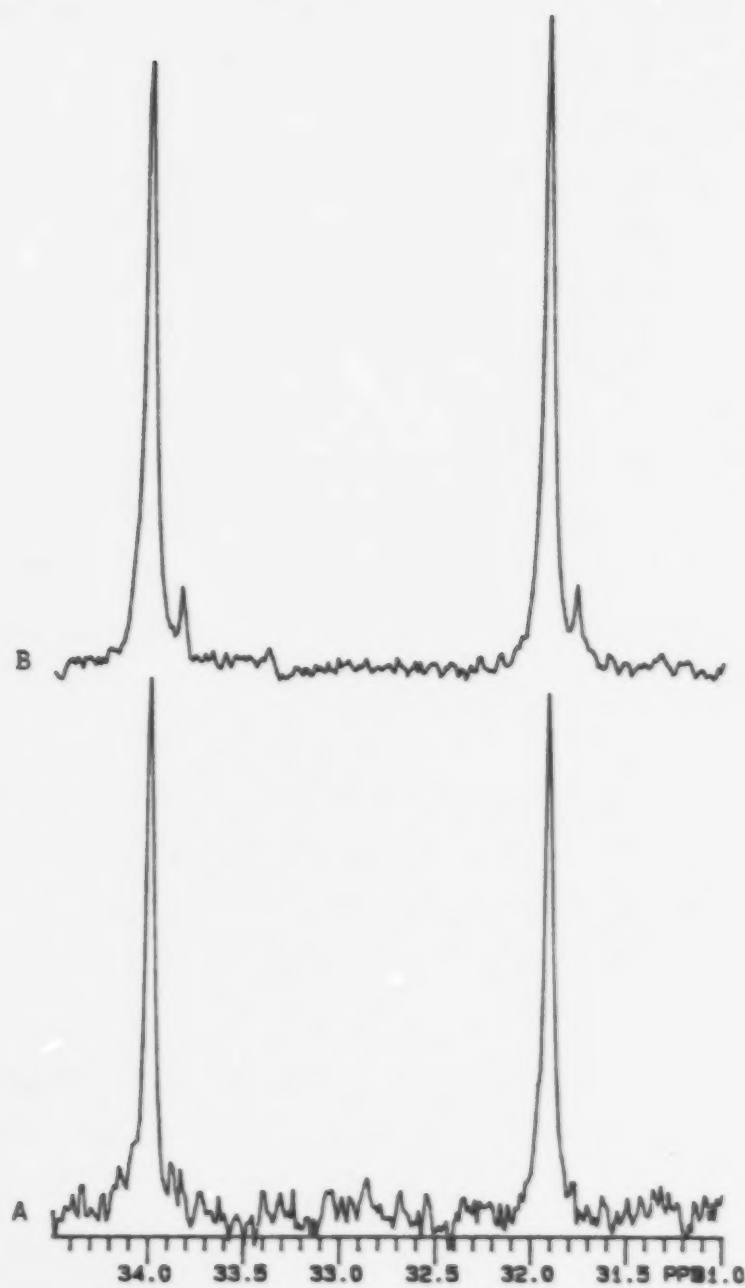
can be assigned to unhydrolyzed P-Cl end groups. Together, both these signals constitute 6.6% of all phosphorus signals. In the blend, the chemical shift of the phosphorus is unchanged for the main phosphonate signal (15.20 ppm), but another signal appears at higher field (7.4 ppm) which is most probably due to the "reacted" phosphonate units. It is to be noted that the end group signals disappeared, indicating that, as in the case of chlorinated polyisobutylene, the end groups are the first to react with the polyurethane. However, the new signal upfield represents now 10.7% of all phosphorus resonance. This means that not only the end groups are active during blending, but that some of the main chain phosphorus is involved also.

Such a high chemical shift (from 18 to 7 ppm for the end groups and from 15 to 7 for the main chain phosphorus) could have consequences in the proton spectrum, also. In order to confirm that the new signal at 4.58 ppm in the proton spectrum of the blend (Figure 5) belongs indeed to the modified MDEA methylene protons and not to the methylene attached to the modified phosphorus, a P-H HETCOR spectrum was run and the chart is presented in Figure 8.

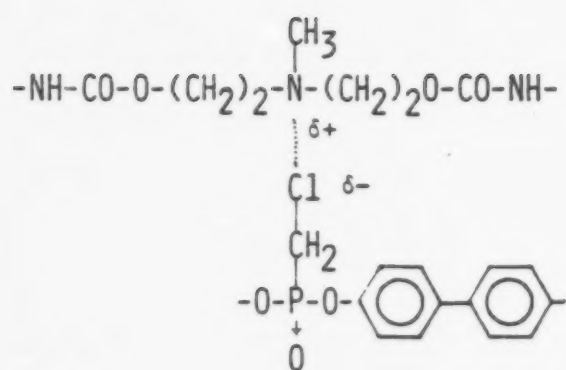
Figure 8

It can be seen in figure 8 that both phosphorus resonances correspond to the main methylene signal at 4.46 ppm in the proton spectrum.

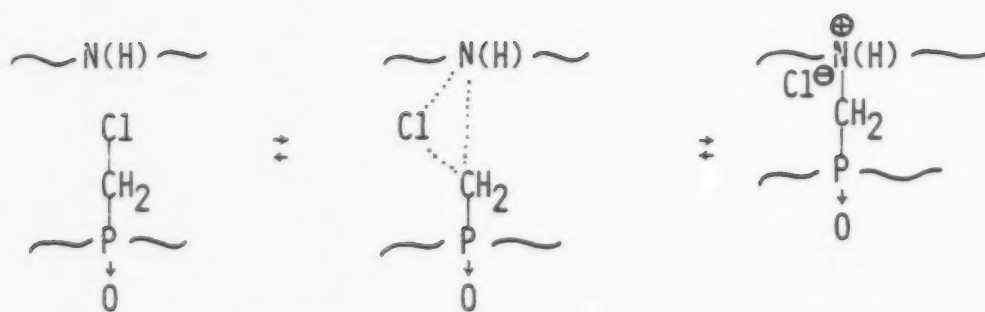
Carbon spectra of the blend and the components show again that some chemical change occurred and that about 10% of the chloromethyl carbons were involved. Figure 9 presents the spectra of the methylene groups in the polyphosphonate (a) and in the



9. Chloromethyl resonance in the ^{13}C -NMR spectra of a) the polyphosphonate and b) the 50% blend in DMSO-d_6 .



SCHEME 2



SCHEME 3



blend (b).

Figure 9

The methylene carbon signal is a doublet, due to one-bond C-P coupling (157 Hz). The reacted methylene carbons also present the doublet having the same coupling constant, but their chemical shift is slightly lower.

Based on these dynamic mechanical and spectral data one can suggest the following mechanism of interaction:

1. Some dehydrochlorination involving the chloromethyl groups of the polyphosphonate takes place. The dehydrochlorination is accelerated by the presence of phosphonic end groups (11) and involves most or all of these end groups. Their involvement is demonstrated by the shift of their signal in the phosphorus spectrum (Figure 7). The hydrochloric acid formed during blend molding can react with the polyurethane nitrogens (8) forming positive charges on the polyurethane, which are neutralized by the chloride anion.
2. Most of the polyurethane nitrogens and polyphosphonate chloromethyl groups are probably involved in a dipole-dipole type attraction, which does not produce spectral changes in the NMR spectra (Scheme 2).

Scheme 2

3. A crosslinking reaction of the type presented in Scheme 3 involves only a small percentage of the polyphosphonate units.

Scheme 3

The main evidence for such a reaction is the shift of about half of the MDEA signals to lower fields, indicating positive charges

on the tertiary nitrogens. This cannot be explained only by end group dehydrochlorination of the polyphosphonate. Also, involvement of more phosphonate units than the end groups, demonstrated by the phosphorus and carbon spectra, supports this hypothesis. The same type of reaction was postulated for blends of polyurethane with chlorinated polyisobutylene (8). The formation of crosslinks is the explanation for the rather small decrease in the high T_g of the blends at higher polyurethane contents.

CONCLUSIONS

Mixing a poly(ether-urethane) with a polyphosphonate produces a phase-separated material. The low T_g phase consists of the polyether part of the poly(ether-urethane). The hard segment of the polyurethane interacts in various ways with the polyphosphonate forming the high T_g phase. The interactions include dipole-dipole interaction and formation of ionic groups by dehydrochlorination and subsequent reaction of the HCl as well as by crosslinking reactions which are also accompanied by Coulombic interaction.

ACKNOWLEDGEMENTS

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Thermal Analysis Studies on Thermoplastic
Rigid Rod Molecular Composites*

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ABSTRACT

Rigid rod molecular composites involve molecular level mixing of two polymers having greatly disparate chain conformations (one rodlike and one flexible coil like). Morphology studies have shown that in such materials the bundle diameter of these rigid rod molecules is less than 50 Å. The rigid rod molecule used is poly-para-phenylene benzobisthiazole (PPBT). The thermoplastic flexible polymer matrix is Nylon 66, DuPont's Zytel 42. Thermal analysis studies on these materials indicate that the expected T_g shifts as observed for blends of two flexible polymers and depression of T_m with increased rod molecule composition do not occur.

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INTRODUCTION

Rigid Rod Molecular Composites (R²MC) have been shown to have outstanding mechanical properties. (1-5) Previous studies have investigated the morphology of these unique materials in an effort to substantiate or vitiate the concept of near perfect molecular dispersion. To date, when the mechanical properties of a processed fiber or film are greatly enhanced over those of the neat host flexible coil matrix polymer, no rigid rod molecular aggregates wider than ~ 50 Å in diameter have been observed. When such a true R²MC system is prepared other so-called synergistic properties have been observed. These include increased solvent resistance and thermal stability. Solvents which previously readily dissolve the host flexible coil polymer do not perceptibly swell the R²MC materials. Additionally, thermal gravimetric analysis (TGA) along with isothermal aging (IA) at elevated temperatures show that the outstanding thermal resistance of the rigid rod reinforcement molecule dominates.

One way to explain these unique properties in terms of molecular morphology is (i) in R²MC systems the very high molecular weight rigid rod molecules dominate the system and therefore the mechanical properties are effectively transferred to the host flexible coil matrix polymer, (ii) since morphologically no aggregates or bundles of rodlike molecules greater than ~ 50 Å are detected, the rigid rod molecules are essentially dispersed in the flexible coil polymer matrix, and (iii) since solvent and thermal resistance of the host flexible coil polymer is enhanced, there must be an intimate association such that the solvent molecules cannot penetrate into the R²MC fiber or film.

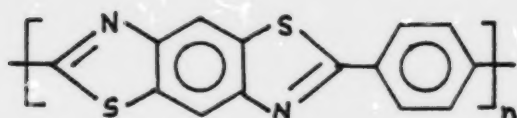
With these facts established, a thermal analysis study was undertaken. If there is such an intimate molecular mixing, one would expect, as in compatible polymer blends, that the T_g of the R²MC should shift as the rigid rod content is increased. This shift could possibly be predicted by use of the Fox-Flory equation (6)

$$\frac{1}{T_g)_{mix}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

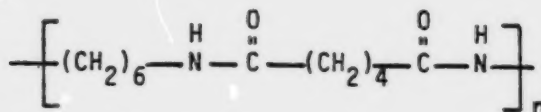
However, this semi-empirical equation was derived for systems where both polymers are flexible coil polymers. In our case, the two polymers have completely disparate conformations. The one is essentially a stiff, straight rigid rod while the other is a flexible or semiflexible coil. If the flexible coil host polymer is semicrystalline, one would expect for a compatible blend system that the melt temperature T_m would be depressed as the rigid rod molecule content would increase. These are the parameters that were studied in this thermal analysis investigation of thermoplastic R²MC systems.

EXPERIMENTALMaterials

The rigid rod polymer poly(p-phenylene benzobisthiazole) (PPBT) with I.V. = 36 dl/g and $M_w = 44,550$ daltons⁽⁵⁾ was obtained from Dr. J. Wolfe, SRI International.

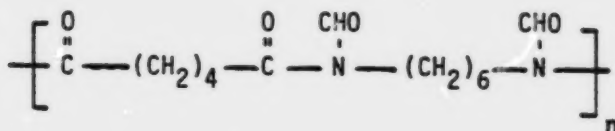


PPBT



Nylon 66

The (poly hexamethylene adipamide) Nylon 66 used in this study is the commercially available Zytel 42 from DuPont. Nominally, its M_w is 70,000 daltons.⁽⁵⁾ An amorphous nylon FE3303 ($M_w = 22,000$ daltons), presently DuPont's Zytel 330, was also used in these studies. The common solvent used for processing films was 98 percent anhydrous methane sulfonic acid (MSA) from Aldrich Chemical Company.



Amorphous Nylon

All specimens studied were codissolved in MSA at about a 3 percent (wt./vol) concentration. The solution was then extruded through a slit die and immediately coagulated in a water bath. After processing, the film or ribbon was washed in running water for at least 48 hours and then pressed together and vacuumed dried while under compression. The processing, coagulation, and drying were all at room temperature.

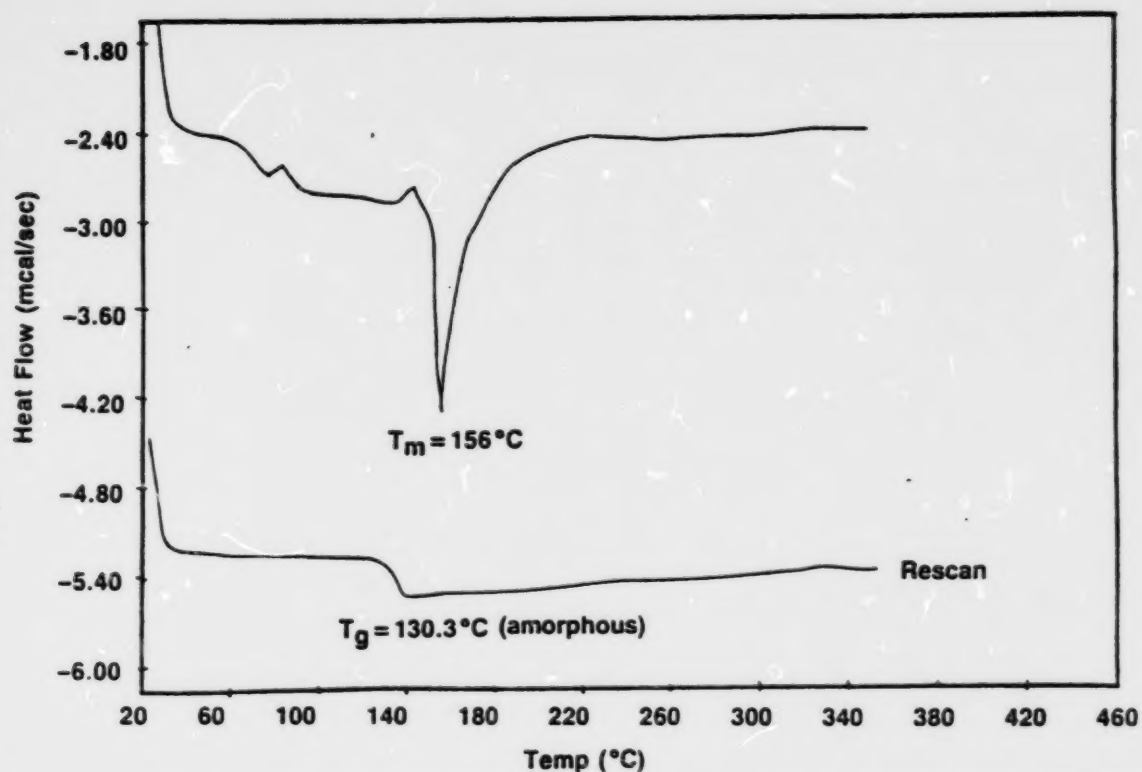


Fig. 1. DSC trace of amorphous nylon FE3303 at a heating rate $10^\circ\text{C}/\text{min}$.

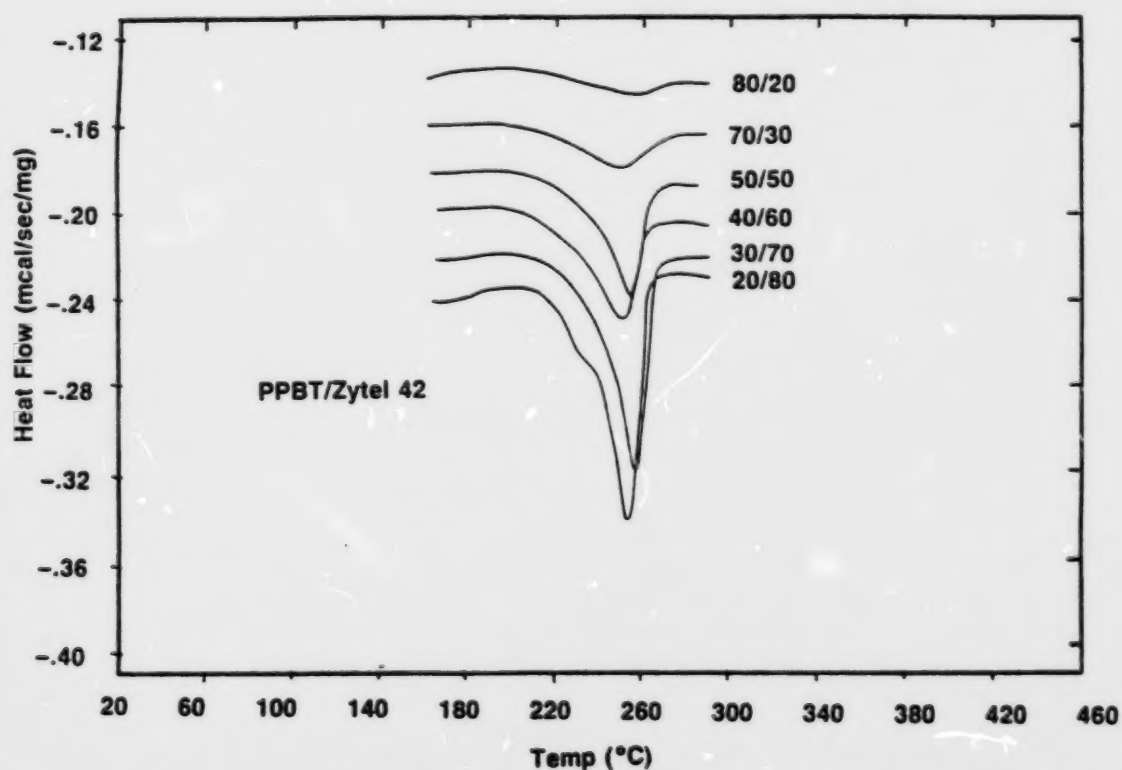


Fig. 2. DSC traces of various compositions of PPBT/Zytel 42 showing melt temperatures.

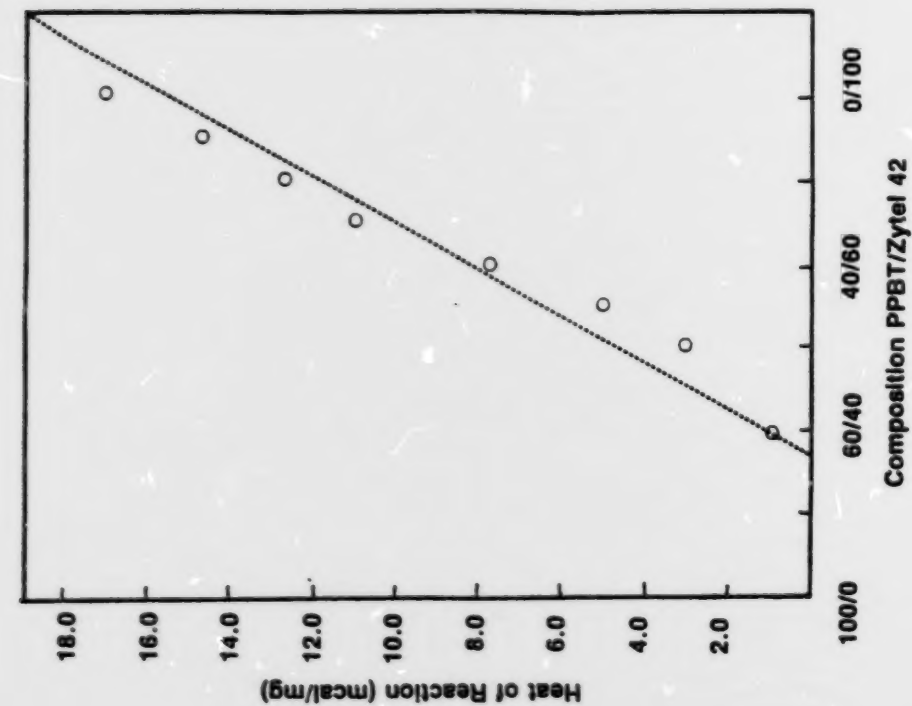


Fig. 3. Heats of reactions from curves of Fig. 2, versus blend composition.

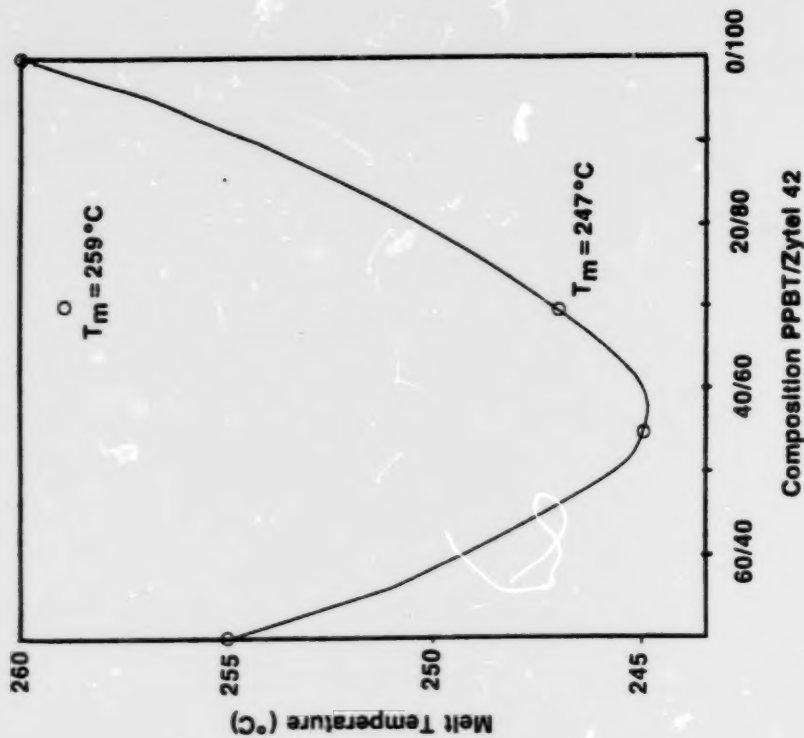


Fig. 4. Melt temperature versus composition for fast coagulated films.

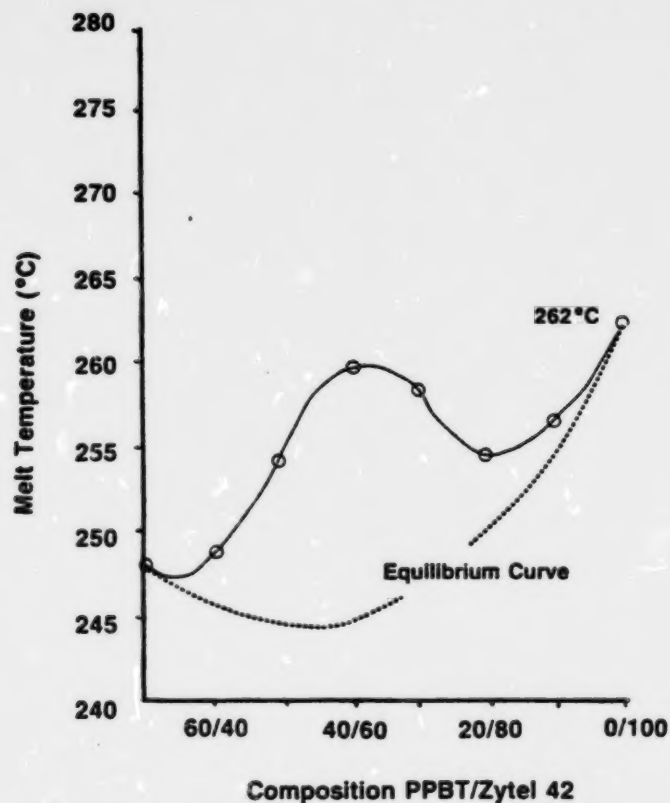


Fig. 5. Melt temperatures versus blend composition for extrudates processed at various shear rates.

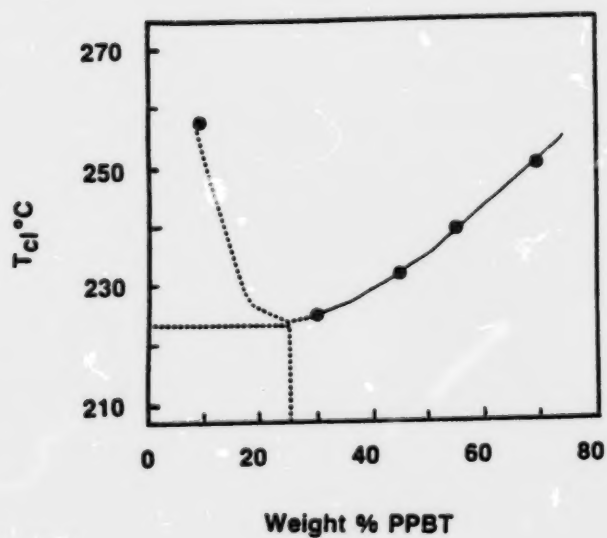


Fig. 6. Cloud point curve of PPBT/Zytel 42 versus composition at heating rate of 5°C/min.

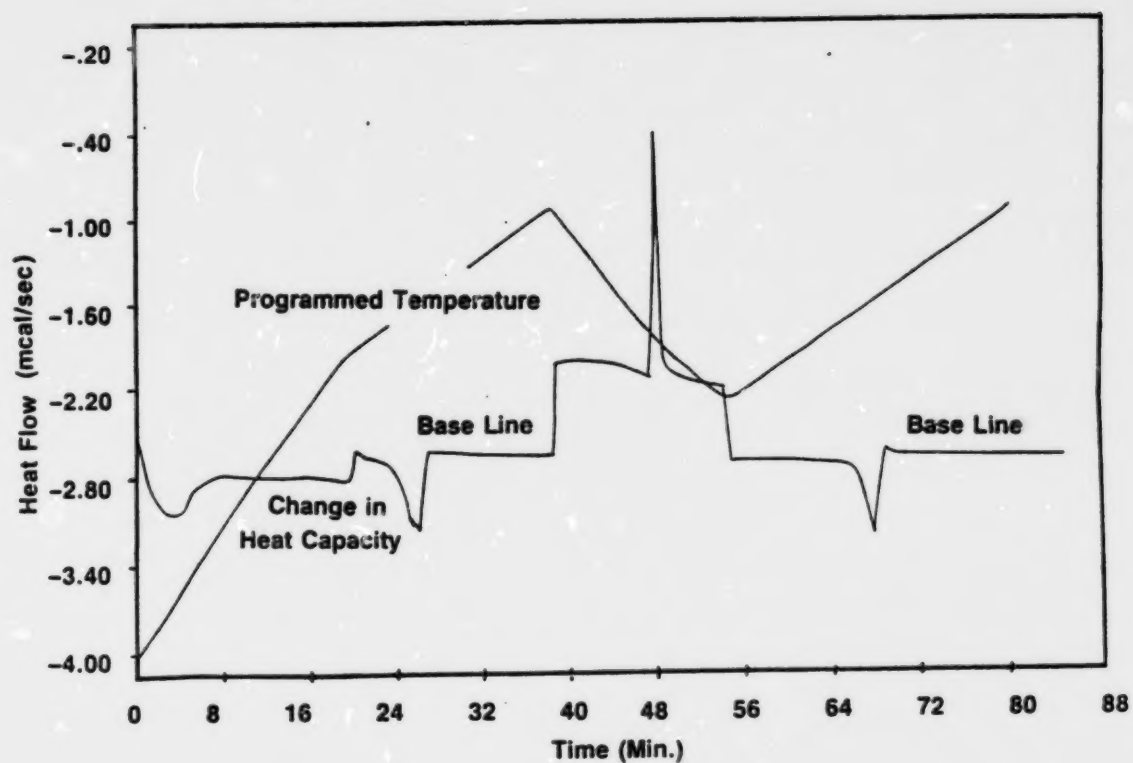


Fig. 7. DSC trace of Zytel 42 using a compression molding temperature profile.

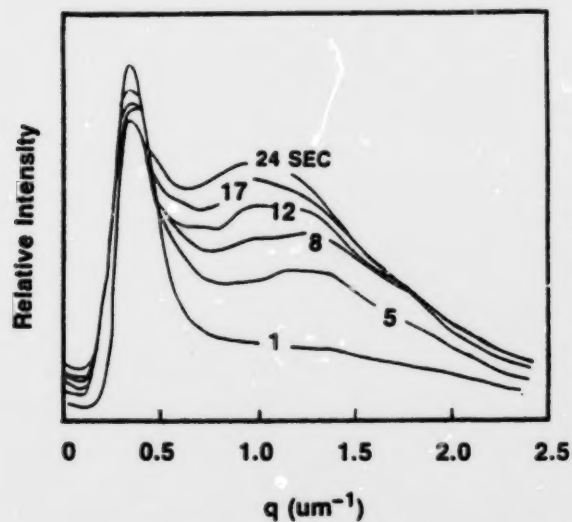


Fig. 8. Scattering curves of a (45/55) PPBT/zytel 42 composition at 260°C and different time intervals.

Equipment

The thermal analysis instrumentation used in the present studies were a DuPont 910 Differential Scanning Calorimeter (DSC), a DuPont 951, Thermal Gravimetric Analyzer (TGA) and a specially fabricated Isothermal Aging (IA) apparatus which periodically weighed specimens over 200 hours while being held at 315°C. All Small Angle Light Scattering (SALS) and optical microscopy studies were performed at the University of Akron using the equipment of Prof. T. Kyu.

RESULTS AND DISCUSSION

Figure 1 presents a DSC scan of an amorphous Nylon (FE3303) sample. The as-received material showed a T_m at 155°C, but upon rescan after initially heating to 350°C, only the amorphous $T_g = 130^\circ\text{C}$ remained. Various compositions of PPBT/Amorphous Nylon were prepared as discussed above in the materials part of the experimentation section. All 5/95, 10/90 and 30/70 (weight/weight) compositions showed an initial $T_m \sim 160^\circ\text{C}$ but additional rescans only exhibited amorphous behavior with $T_g \sim 130^\circ\text{C}$ for the 5/95 and 10/90 samples and $T_g \sim 127^\circ\text{C}$ for the 30/70 composition. Six similar samples, 20/80, 30/70, 40/60, 70/30 and 80/20 compositions (wt/wt) of PPBT/Zytel 42 were prepared and examined for T_m (Figure 2). In Figure 2, the ordinate has been normalized for sample weight. Heats of reaction were determined for each of these curves and the results are presented in Figure 3. The plot is linear indicating a physical mixture. If there were entanglement effects, we would not have obtained a straight line. This is in agreement with previous morphology investigations.⁽³⁾ When the melt temperatures were plotted versus PPBT composition, Figure 4 was obtained. At the 30/70 composition, a new sample was prepared, but being in a hurry the solution (PPBT/Zytel 42 in MSA) was spread on a glass (as with a Doctor Blade) and immediately coagulated, washed and dried. The melt temperature for this sample was 259°C. An interpretation for this is that now there is phase separation due to the shearing which occurred during sample preparation. However, a previous study of morphology and rheology on various molecular weights of reinforcement (PPBT) yielded a series of samples extruded at various shear rates from an Instron Capillary Rheometer.⁽⁵⁾ The results of T_m determinations as a function of PPBT composition are shown by the solid line in Figure 5. The dashed curve follows the curve from Figure 4 for unstrained samples.

Cloud point determinations allowed us to draw the phase diagram shown in Figure 6. This looks like an LCST (25 percent PPBT and 225°C) but since the rods and coils are forced together through coagulation, there is no "true" LCST. From DSC studies the melting endotherm for a composite (PPBT/Zytel 42) begins at about 225°C and is broad. Thus, phase separation occurs with the onset of chain mobility on melting. The temperature at which this occurs depends on the rod content and the frozen-in strain in the sample. Mechanical properties reported in previous publications were associated with materials where there was a minimum of phase separation. Compression molding of samples was achieved by keeping the temperature near but below the melt temperature. This allowed compacting and reduced the chances of phases separation.

To test this, the DSC was programmed to follow a compression molding cycle (Figure 7). We knew from SALS studies (Figure 8) that within 24 seconds large phase separation occurred when the sample was at or above the melt

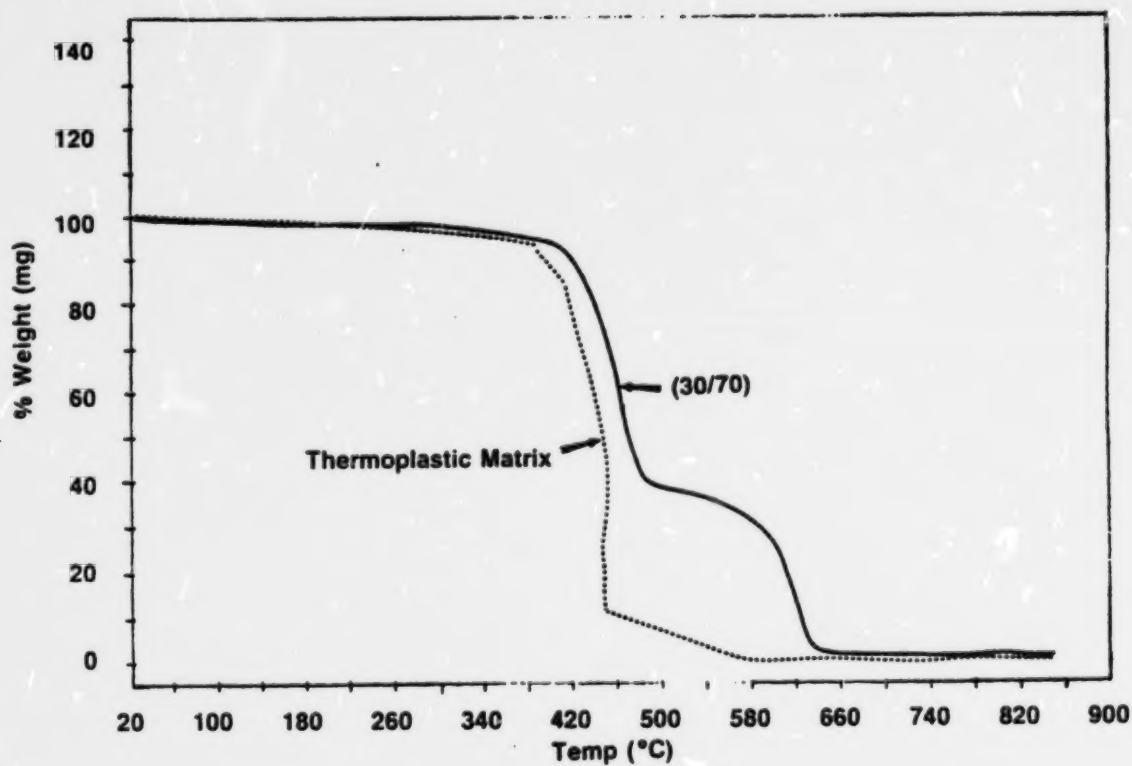


Fig. 9. TGA of a 30/70 composition of a molecular composite compared to the neat matrix.

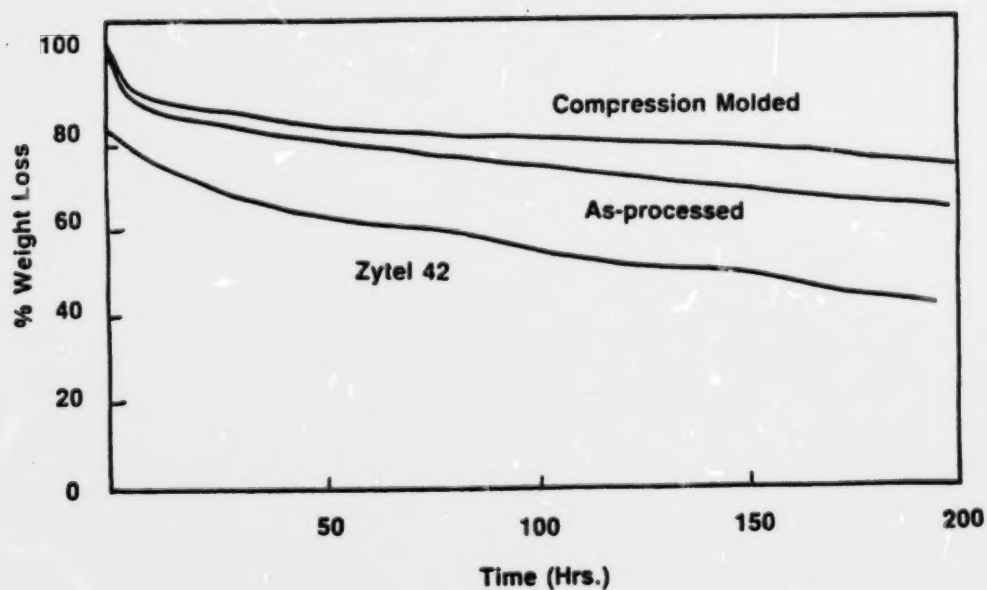


Fig. 10. Isothermal aging curves for compression molded, as processed and neat thermoplastic matrix samples.

temperature. As reported by Wunderlich,⁽⁷⁾ only when overall molecular conformation equilibrium is reached is the DSC curve independent of temperature (flat). In Figure 7, these regions are designated as baseline for 100 percent Zytel 42. When studies were made on PPBT/Zytel 42 compositions, cycling of the temperature up and down through the melt relaxed strain induced by the fast coagulation. The temperature cycle was between 200° and 325°C at a heating rate of 10°C/min. This was done for a 30/70 composition of a processed film and a hand sheared quickly coagulated film. In all cases after the first cycle, the baseline was flat. However, in the first cycle, the highly sheared quickly quenched film showed the least amount of induced strain. This can be attributed to the thinness of the film and thus how quickly the coagulation process occurs. As mentioned above with regard to Figure 4, the highly sheared quickly coagulated film of the 30/70 composition had the higher melt temperature. This helps us understand that even the high shear rate samples produced with the capillary rheometer (Figure 4)⁽⁵⁾ showed variations in T_m depending on coagulation time. As seen in SALS studies this time is less than thirty seconds.

CONCLUSIONS

As indicated in the introduction, a rigid rod thermoplastic molecular composite is a molecular level dispersion of intrinsically rigid rod polymers dispersed in a flexible and/or semiflexible coil-like polymer matrix. When the matrix is a crystalline polymer, one would expect to detect a T_m . If the matrix is amorphous there would be a T_g . Both T_m and T_g should vary with composition if we have an intimate molecular level mix. In all cases, it appears that the T_g and T_m remains unchanged. X-ray diffraction studies indicate a third phase does not occur but after heat treatment, there is a 5.9 Å intermolecular PPBT spacing present. On the other hand, SEM, TEM and STEM examinations show that there are no PPBT rod molecule bundles larger than - 50 Å.⁽³⁾

In the present case, the very long (high molecular weight) rigid rod molecules dominate the entire mixture of rigid rod/flexible coil polymers. These long molecules give the solution more rigidity and/or integrity (Figures 9 and 10). At low and high temperatures, they exemplify themselves in the outstanding mechanical properties of R²MC systems. After heat treatment, the 5.9 Å intermolecular PPBT spacing is probably a result of the low molecular weight PPBT phase separating during coagulation from essentially a coacervated concentrated solution. Usually, one thinks of the high molecular weight rigid rods phase separating first as in liquid crystalline systems. Here, however, the long molecules are essentially immobilized in a highly viscoelastic media. On the local molecular level where the polymer segments are influenced only by their neighbors with regard to T_g , there is no perceptible influence of a long intrinsically rigid molecule penetrating the local environment. As the temperature is increased only the flexible coil segments move; the rigid rod molecule cannot flex. Any influence the long rod molecule has on a local molecular environment is essentially too small to be experimentally detected by the DSC. Similarly, crystalline polymers containing crystallites will be undisturbed on a local level with regard to melting except when strained, thus causing microdomain crystallites.

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CHARACTERIZING POLYETHYLENE BASED BLENDS WITH TEMPERATURE
RISING ELUTION FRACTIONATION (TREF) TECHNIQUES

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ABSTRACT

The temperature rising elution fractionation (TREF) technique makes use of the differential crystallizabilities, introduced by short chain branches (SCB), to enable one to physically fractionate polyethylenes (PE) on the basis of the SCB level of any one chain. This allows one to probe the SCB distribution of a polymer. The TREF technique has been applied to blends of PE by recognizing that the two commercial types of low density polyethylene, high pressure (HP-LDPE) and linear low density (LLDPE), have different short chain branching distributions. As well, other common copolymers of ethylene, like ethylene vinyl acetate (EVA) or terpolymers like ethylene/propylene/hexadiene (EPDM), have different SCB types, levels and distributions and will therefore have different TREF behaviour. We have constructed a TREF apparatus which can be used in a number of different types of blend studies. The first is an Analytical-TREF which gives a profile of the amount of polymer with a given SCB level and can be used to quantify HP-LDPE/LLDPE blends. We have also modified the technique to construct a stop-flow TREF apparatus which enables one to separate fractions on the basis of the branching levels. The fractions can then be analyzed by size exclusion chromatography, IR, ^{13}C NMR or DSC. The use of these TREF techniques to characterize blends of HP-LDPE/LLDPE, LLDPE/EVA, PE/EPDM and PE/polyisobutylene is discussed.

INTRODUCTION

In recent years there has been considerable effort devoted to the study of polyethylene based blends. In part, this is the result of a desire to modify certain properties (stiffness, toughness, melt strength etc.) of the relatively inexpensive polyethylene in order to enable it to perform in different applications and environments. While it is generally very easy to determine the types of comonomers present in a sample of polymer by ^{13}C NMR or IR it is often difficult to determine whether the material is one polymer or a blend of two or more components. In order to aid in quantifying the composition of known blends, and to determine and quantify the structures of components in unknown blends, we have begun to apply the temperature rising elution fractionation (TREF) technique to blends based on polyethylene.

The TREF technique makes use of the differential crystallizabilities, introduced by the short chain branches (SCB), to physically fractionate a PE sample on the basis of the SCB level of any one chain (1-6). In a TREF fractionation, the sample is dissolved in a solvent (xylene(1), trichlorobenzene(2,3), o-dichlorobenzene(4,5) or α -chloronaphthalene(6)) and allowed to slowly cool to room temperature in a column loaded with an inert support. During this cooling, PE chains with low branching levels are deposited first, followed by chains with increasing SCB levels. The polymer is then taken off the column, in the inverse order in which it was deposited, by simultaneously heating and eluting the column with solvent. In an Analytical-TREF, of the type

described by Wild et. al. (2), the concentration of polymer in the eluting solvent can be determined with a refractive index detector (2) or an IR detector (6) and a profile of the quantity of polymer versus elution temperature can be constructed. This can then be converted to a profile of the SCB level, by using a calibration prepared from known, narrow SCB distribution resins or fractions (2,6).

The Analytical-TREF has been instrumental in demonstrating that there is a bimodal intermolecular SCB distribution in linear low density polyethylene (LLDPE). By contrast, high pressure-low density polyethylene (HP-LDPE) exhibits only a single peak in the Analytical-TREF, indicating a homogeneous intermolecular distribution of short chain branches. Because of the profound differences in the shapes of the Analytical-TREF profiles for LLDPE and HP-LDPE it has been shown that it is possible to characterize blends of these two types of polyethylenes (7). In favourable circumstances, especially when the densities are different, it is possible to separate them completely. By extension, any polymer with suitable solubility (ethylene-vinyl acetate (EVA), ethylene-ethyl acrylate (EEA), ethylene/propylene/hexadiene terpolymer (EPDM), polyisobutylene (PIB), polypropylene (PP) etc.) will have a characteristic Analytical-TREF profile, depending upon its crystallization behaviour in the solvent system being used. The remainder of this paper reports on the use of Analytical-TREF and other TREF techniques to quantitatively characterize, or separate, blends of different types of polyethylenes (HP-LDPE and LLDPE) as well as blends of many other materials with different polyethylenes.

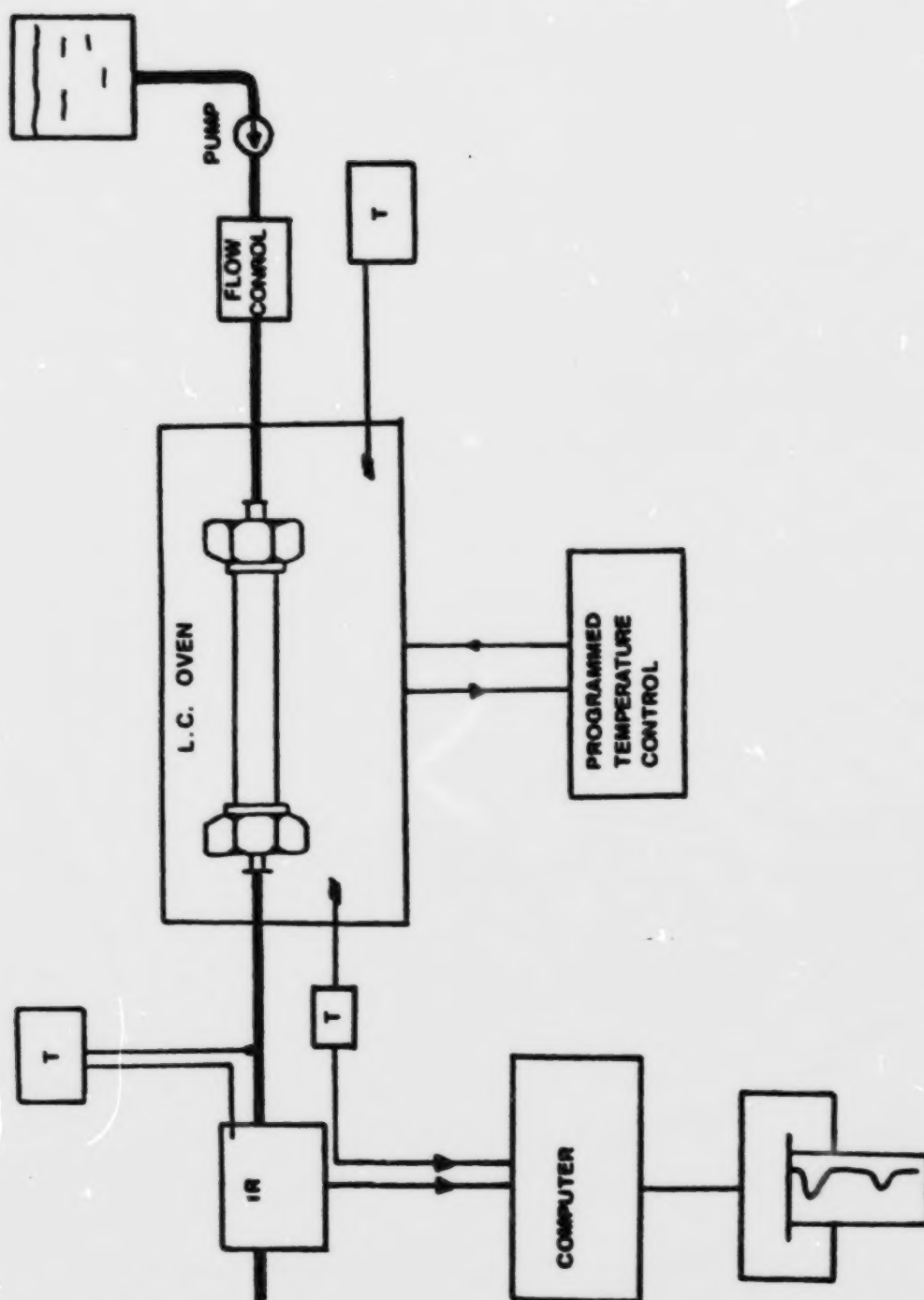


Figure 1.) Schematic of the Analytical-TREF apparatus(6) used for SCB distribution studies.

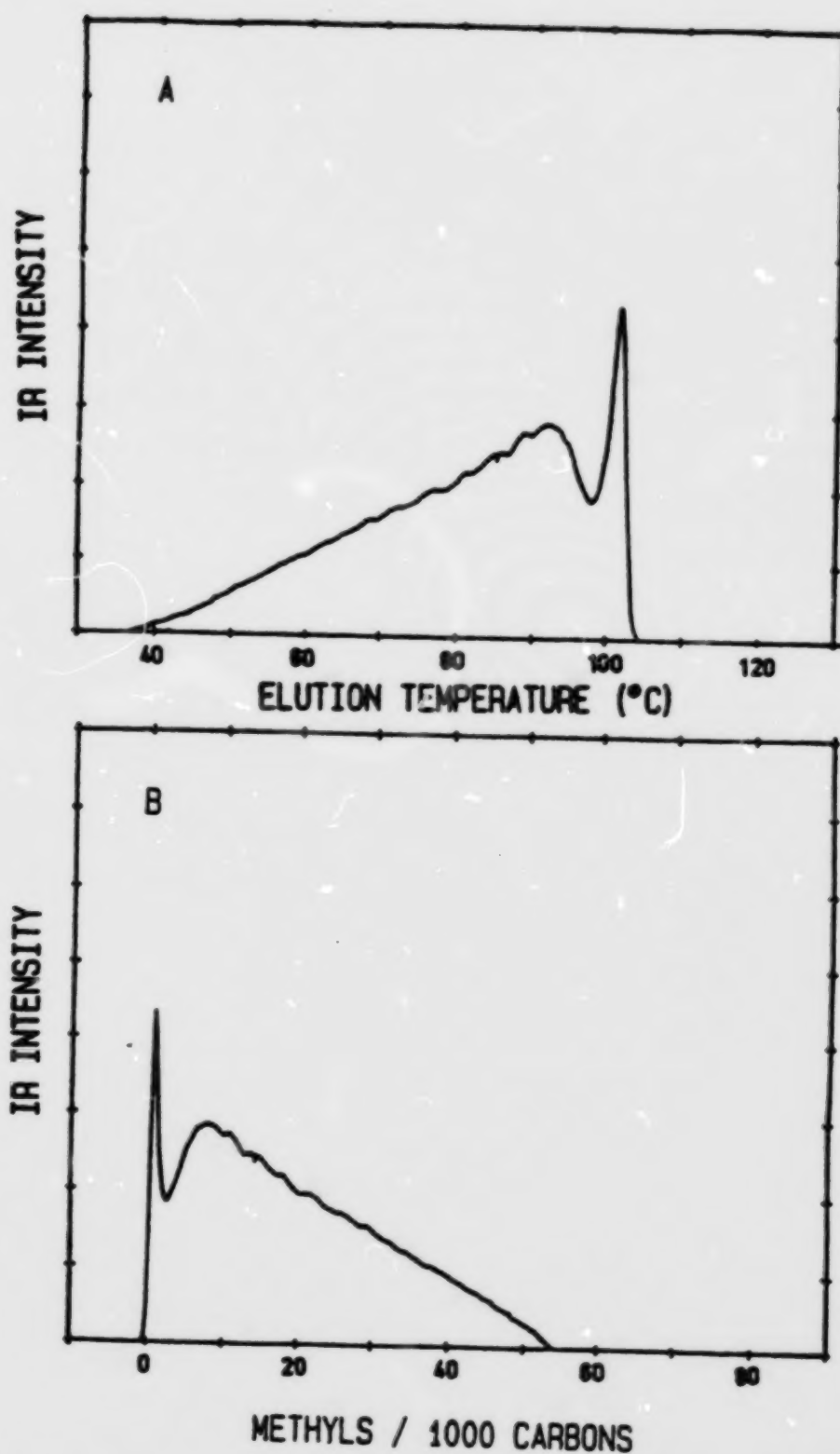


Figure 2.) (A) TREF profile of polymer concentration (by IR) versus the elution temperature. (B) Polymer concentration versus total methyls obtained from A.

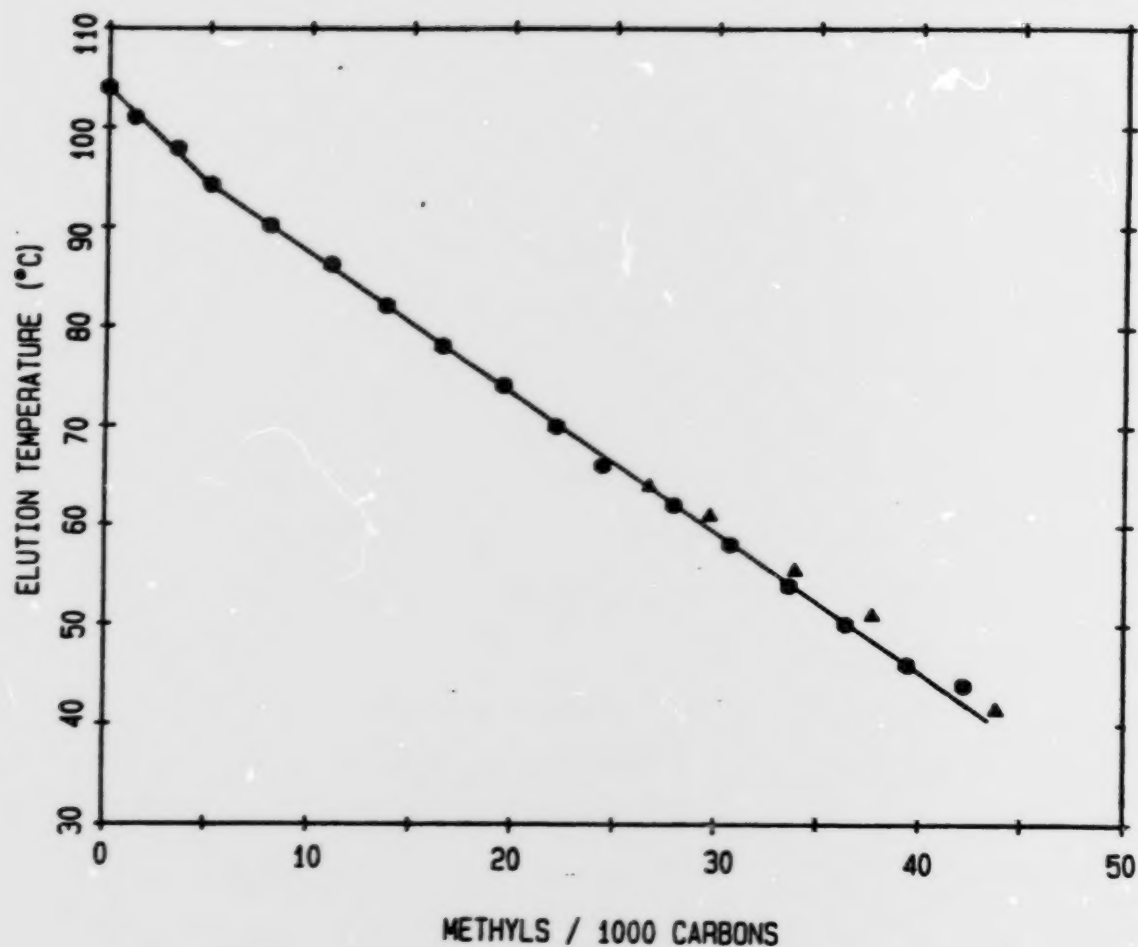


Figure 3.) Calibration curve relating the elution temperature to the number of methyl groups/1000 carbons. Methyl groups represent the sum of short chain branches and chain ends. The calibration curve was constructed (6) from narrow fractions taken from an ethylene/butene LLDPE (●). The triangles (▲) represent the data points for the HP-EVA resins (see Table 1).

EXPERIMENTAL

The TREF system used in this work has been described previously in detail (6) and a schematic of our Analytical-TREF is shown in Figure 1. In a typical experiment, a solution of the polymer in α -chloronaphthalene is loaded onto a column packed with an inert support and allowed to cool slowly to room temperature. The column is then eluted with α -chloronaphthalene and both the column and solvent are heated at a fixed rate. The concentration of the eluting polymer is measured with an IR detector. The temperature and IR intensity data are transferred to a computer for subsequent data manipulation. With the IR/elution temperature data on the computer, it is also possible to add or subtract Analytical-TREF profiles using a number of FORTRAN programs which we have written. This allows us to simulate the expected TREF profiles of a blend by adding appropriate percentages of the pure components. Alternatively, one can subtract the TREF profile of one component of a blend to obtain the profile of the second component.

A typical plot of polymer concentration versus elution temperature is shown in Figure 2A. This can be converted to a profile of polymer concentration versus SCB level (Figure 2B) using a previously determined calibration (6) which is based on narrow fractions taken from an ethylene/butene LLDPE (Figure 3). This calibration actually relates the elution temperature to the total methyl content of a polymer chain. The total methyls is the sum of the number of short chain branches and the

number of end groups, since an end group has the same influence in a TREF experiment as a branch (2). While it is very simple to convert from elution temperature to SCB levels in branched polyethylenes, it is less meaningful in blends containing species other than polyethylene. This is because the elution temperature/SCB correlation, which was determined for polyethylene, will not necessarily apply to other polymers. Consequently, only the elution temperature profiles will be shown.

The Analytical-TREF described above can also be reconfigured to perform large scale, stop-flow TREF experiments (6). In this experiment, a column capable of holding 0.75 g of polymer is used. Rather than continuously heating, eluting and monitoring polymer concentrations, the stop-flow experiment collects fractions over narrow temperature intervals. These fractions are collected, precipitated with methanol and then analyzed by DSC, IR, SEC, ^{13}C NMR etc.

^{13}C NMR spectra, for branching analysis, were obtained at 120°C on a Bruker CXP-200 operating at 50 MHz. Samples were made up in trichlorobenzene (15% w/v) and run in 10 mm tubes with a 4 mm inner tube containing diglyme- d_{14} as a lock solvent. Spectra were acquired with 60° pulses and 8 second recycle times.

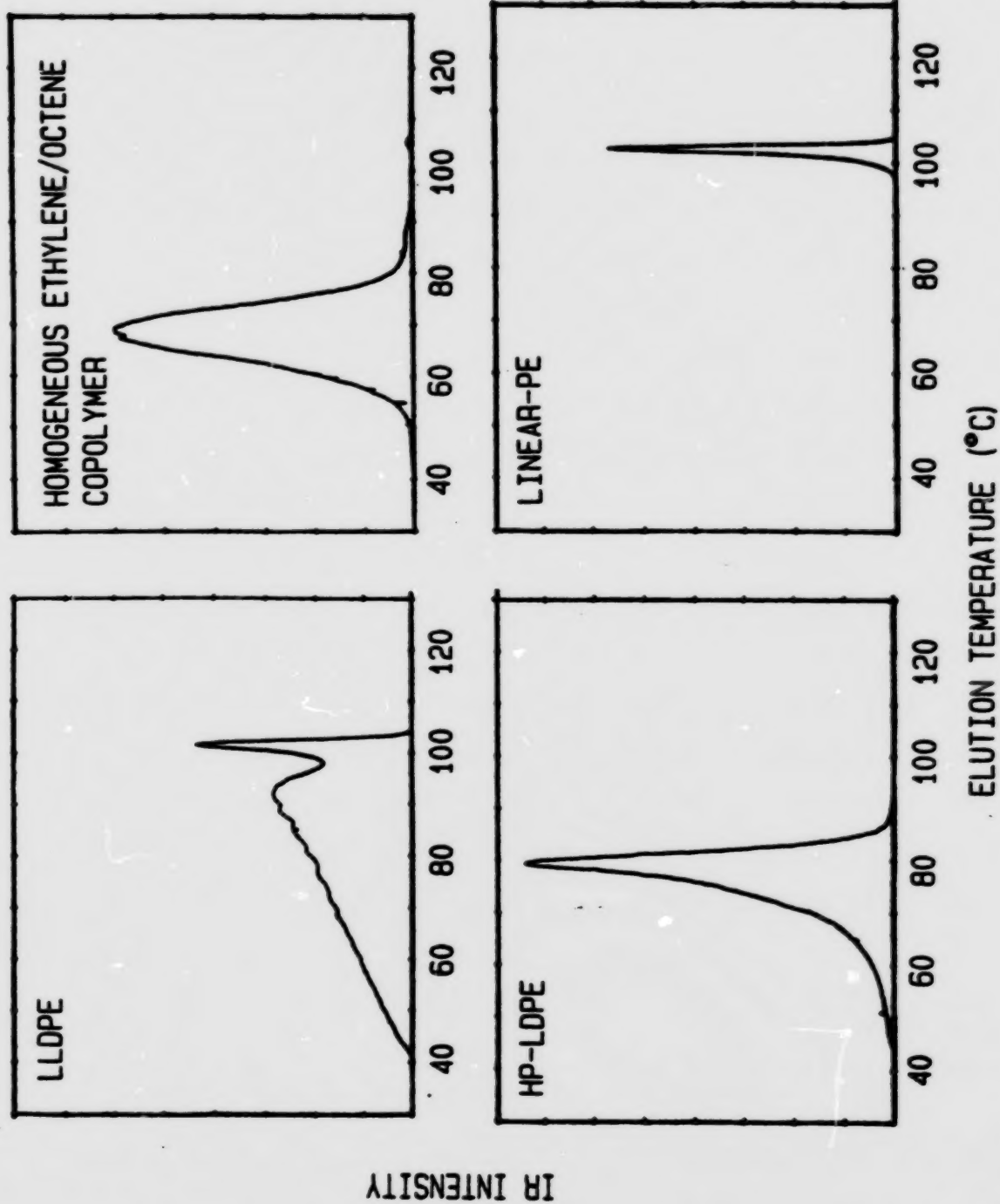


Figure 4.) Analytical-TREF profiles for common types of polyethylenes.

RESULTS AND DISCUSSION

A. Characterization of Polyethylene Types

Figure 4 shows the Analytical-TREF profiles of four different types of polyethylenes; a commercial LLDPE, a commercial HP-LLDPE, an experimental ethylene/octene copolymer made with a soluble homogeneous catalyst and a linear polyethylene. The inherent difference between HP-LLDPE and LLDPE is immediately apparent from the Analytical-TREF profiles. The LLDPE shows a bimodal distribution characterized by a broad peak, going from 42-100°C, which comprises the SCB containing chains and a second peak at 103°C which is essentially a linear component. This peak corresponds exactly with the TREF profile of the linear polyethylene. The bimodal distribution has been interpreted as resulting from two different types of sites in the catalyst (5), one of which only accepts ethylene. This bimodal shape has been observed in LLDPE resins produced with a number of different catalysts and in different commercial processes (2,3,5).

For the HP-LDPE sample there is only a single, narrow TREF peak reflecting a homogeneous intermolecular SCB distribution, that is, all of the chains have essentially the same branching level. Since there are many different types of branches found in HP-LDPE resins (8), the homogeneous TREF profile indicates that the total SCB (C_1 through C_6 branches) level exhibits an intermolecular homogeneity. This homogeneity is a consequence of the free radical mechanism which occurs in the HP

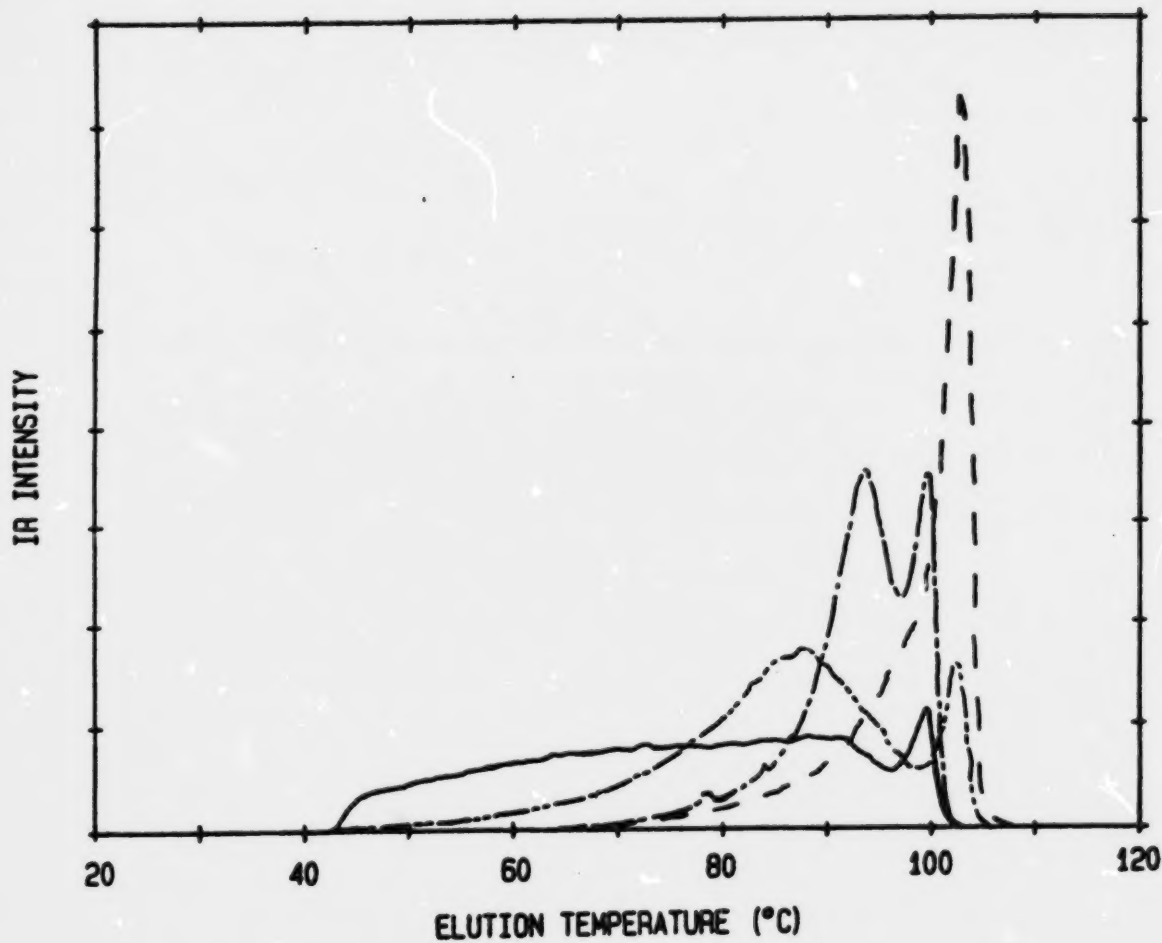


Figure 5.) Influence of comonomer content (density) on the TREF profiles of LLDPE.

- | | | |
|-----|---------|-------|
| (A) | = 0.941 | ---- |
| (B) | = 0.935 | -.-.- |
| (C) | = 0.919 | |
| (D) | = 0.909 | ———— |

polymerization process. Most of the commercial HP-LDPE resins which we have examined also show a substantial low temperature tail (like that seen in Figure 4). This likely reflects non uniformity within the HP polymerization process.

The homogeneous copolymer was prepared with a soluble vanadium catalyst (9-11). This catalyst appears to lack the sterically restricted sites found in the commercially used LLDPE catalyst and as a result it does not produce the 'linear' component present in the commercial LLDPE resins. The width of the distribution is still broader than that found for the HP-LDPE resin, however the distribution is more symmetric than in the HP resin.

Finally, the influence of comonomer level on the shape of the Analytical-TREF profile for a series of ethylene/butene LLDPE resins is shown in Figure 5. As the amount of butene is decreased, the broad component becomes smaller and moves to progressively higher temperatures until it almost merges with the linear component. By comparison, the linear polyethylene shown in Figure 4 has only a single, very narrow peak at 104°C.

B. HP-LDPE/LLDPE Blends

Blends of HP-LDPE and LLDPE have found wide application in the production of films. While it is generally very easy to identify the presence of HP-LDPE by ^{13}C NMR, it is impossible to obtain an accurate measure of the type or level of HP-LDPE in a blend. DSC can be used in

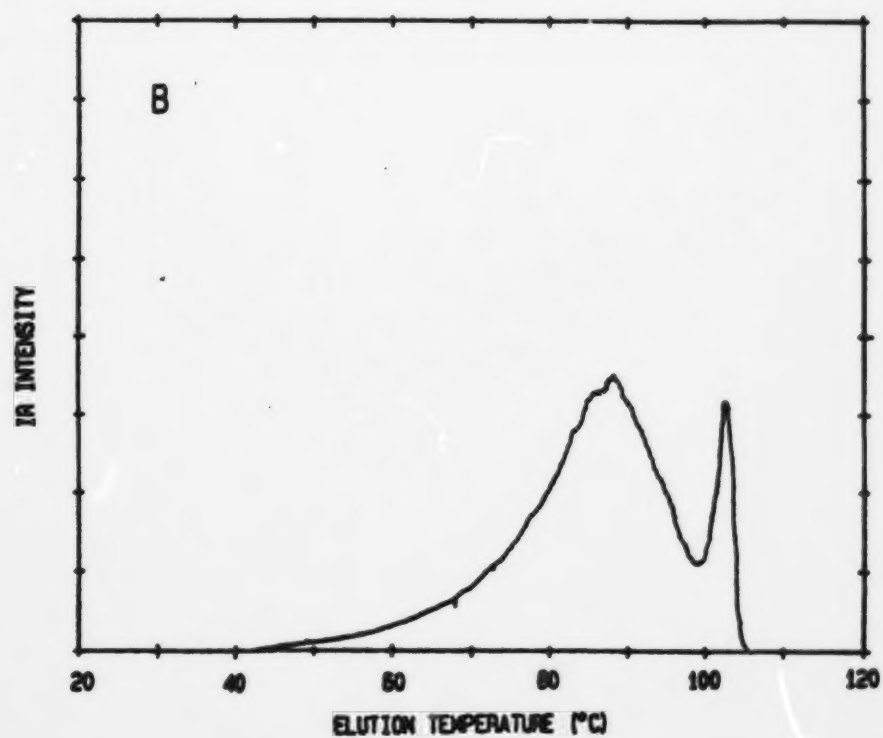
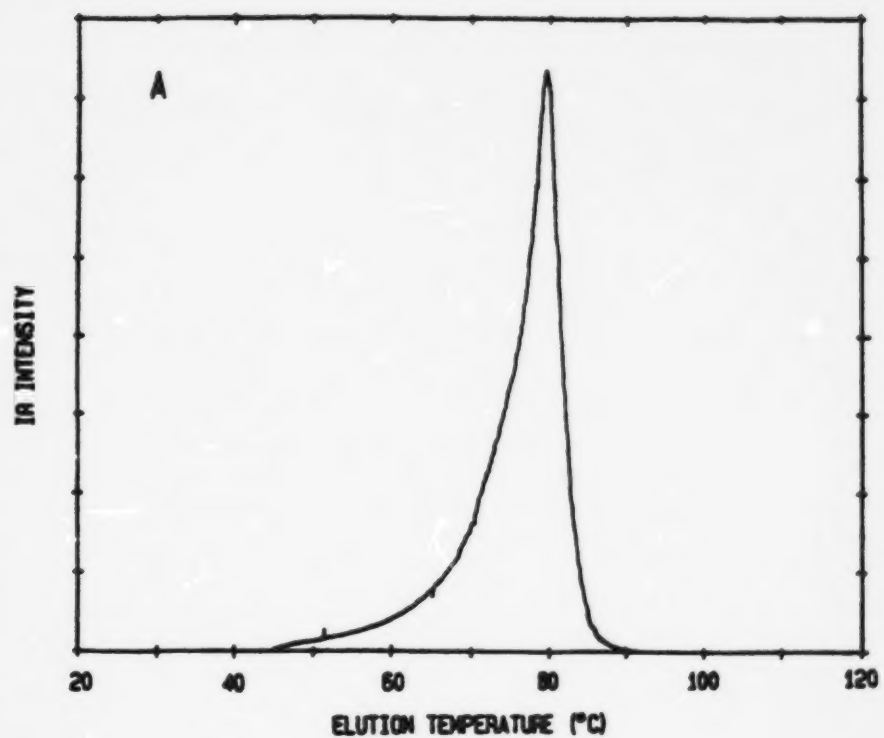


Figure 6.) Analytical-TREF profiles of (A) a HP-LDPE and (B) an ethylene/butene LLDPE polymers.

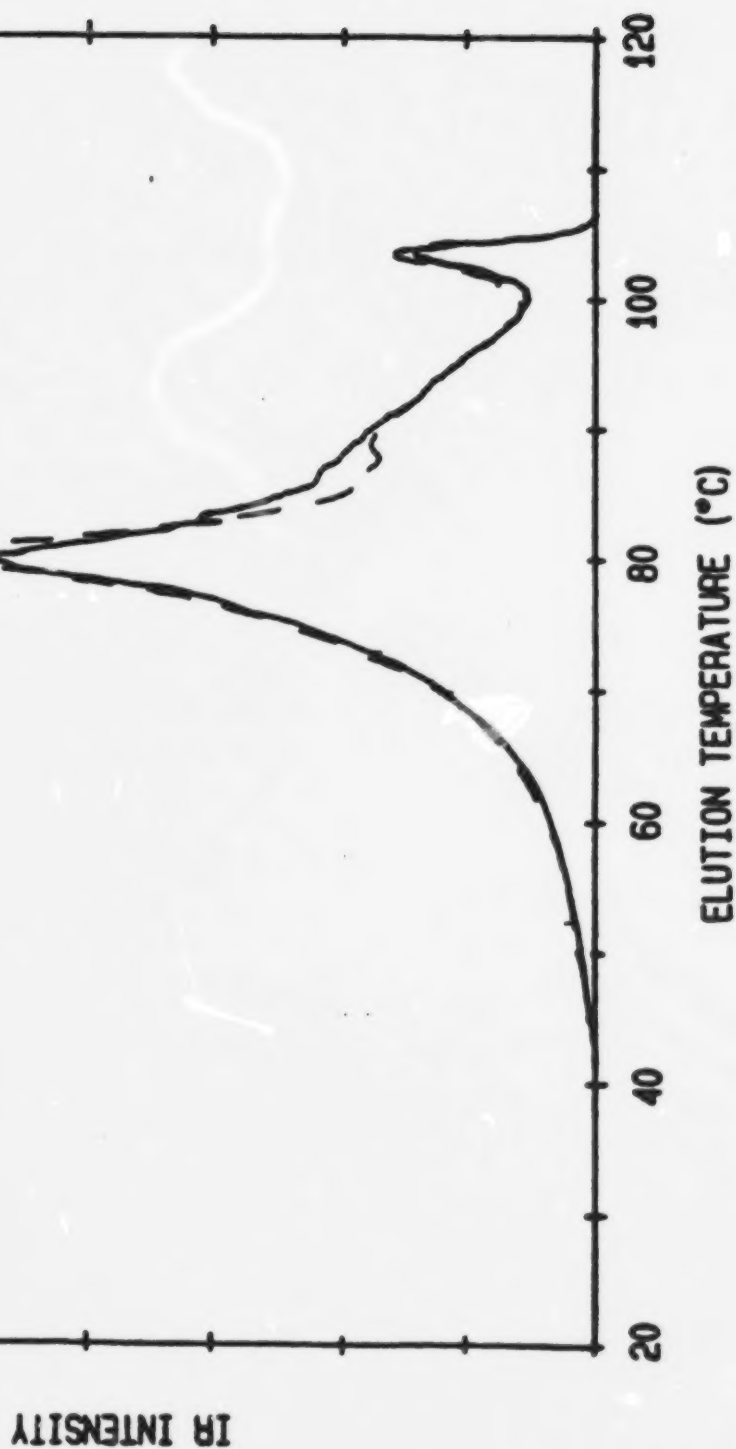


Figure 7.) Analytical-TREF of a 50/50 blend of the HP-LDPE and LLDPE shown in Figure 6. Actual blend (—). Predicted blend (---) based on a 50/50 summation of the two TREF profiles in Figure 6.

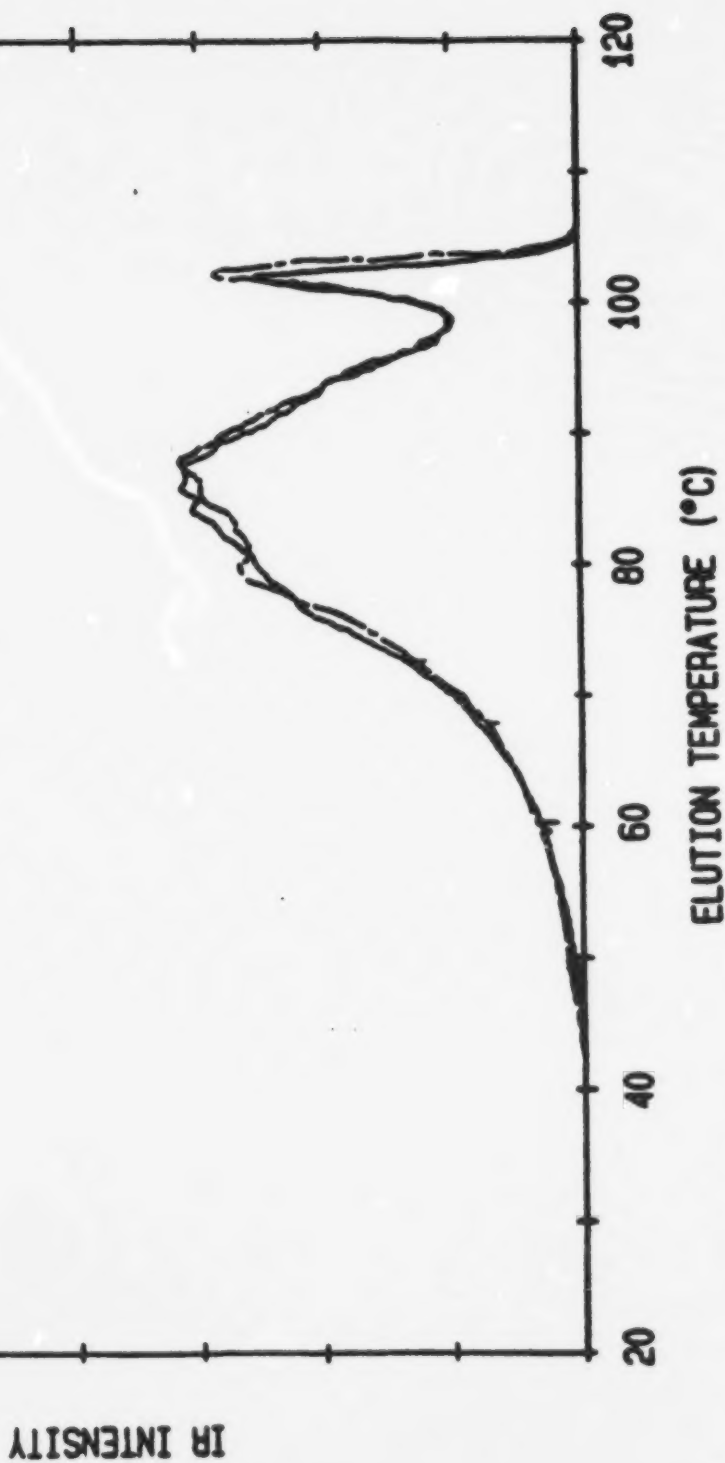


Figure 8.) Analytical-TREF of a 10/90 blend of the HP-LDPE and LLDPE shown in Figure 6. Actual blend (—). Predicted blend (---) based on a 10/90 summation of the two TREF profiles in Figure 6.

very favourable cases to quantify the amount of LLDPE and HP-LDPE in blends of the two components. However, unless the two components of the blend can be obtained separately, there is a large uncertainty in the values obtained from the DSC technique. From the differences in the Analytical-TREF profiles shown in Figure 4, it is clear that blends of HP-LDPE and LLDPE will be resolved by TREF.

Figure 6 shows Analytical-TREF profiles of a LLDPE (ethylene/butene with 14.4 branches/1000 total carbons) and a HP-LDPE (25.2 branches/1000 total carbons) typical of those used in film production. The profiles are normalized to give equal areas under the curves. Figures 7 and 8 show the Analytical-TREF profiles obtained for 50/50 and 10/90 blends (HP-LDPE/LLDPE) of the components as well as profiles obtained by summing the appropriate percentages of the pure component profiles shown in Figure 6. In both cases, the HP resin can be seen as a low temperature peak or shoulder on the LLDPE profile. While the summations show a generally good agreement with the actual experimental blends, there is a slight shift of some of the HP intensity from the centre of its pattern (79.5°C) to the 83-88°C range. This shift in intensity appears, to some extent, in all of the HP-LDPE/LLDPE blends we have examined, but not in the EVA/LLDPE blends (to be discussed later). It may be that this represents the best resolution we can achieve in these circumstances, however tests of resolution and reproducibility suggest that this is not likely the case. It is also possible that the crystallization of a small portion of the HP-LDPE component is being influenced by the LLDPE. If HP-LDPE chains exist, which have structural

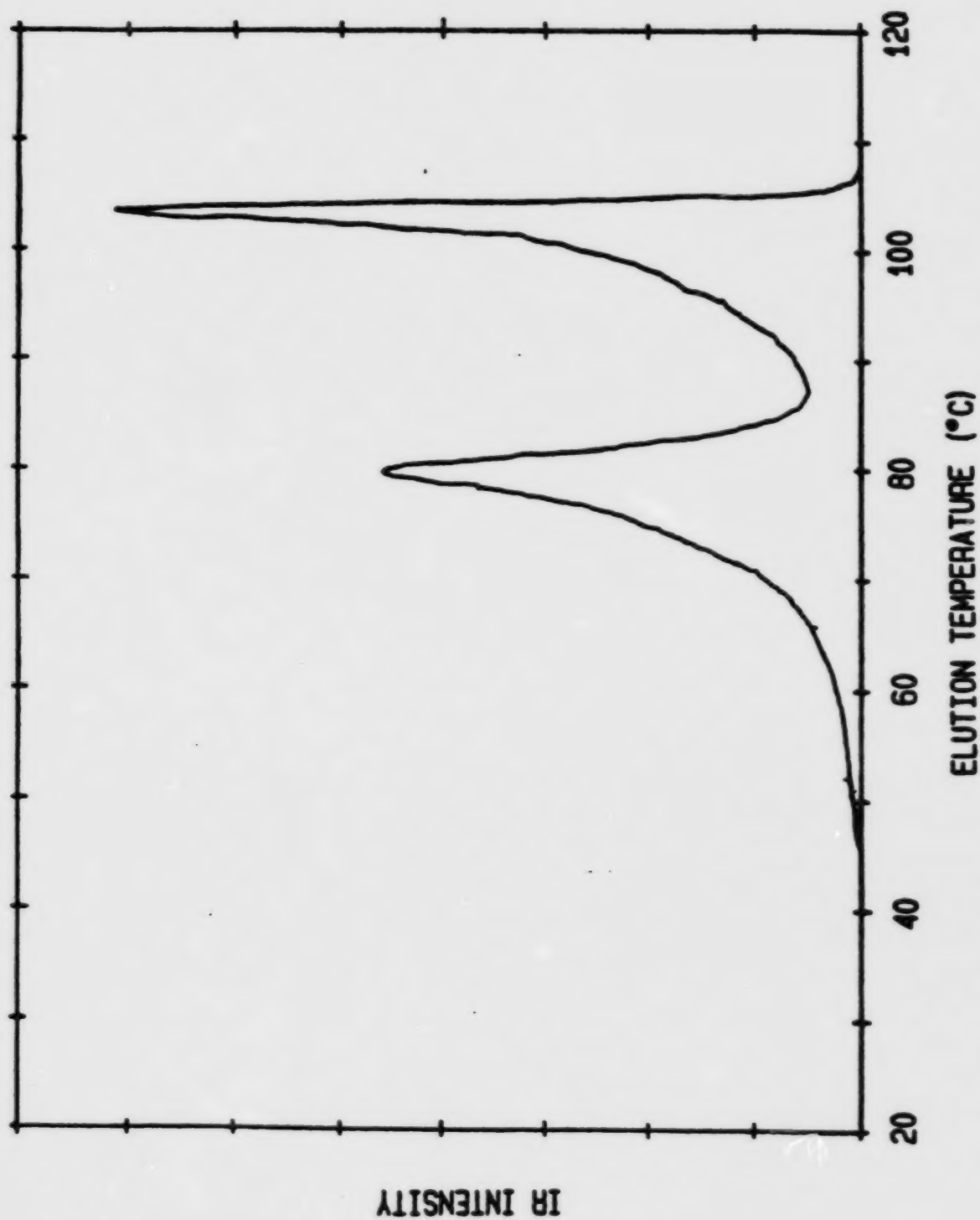


Figure 9.) Analytical-TREF of a 50/50 blend of the HP-LDPE shown in Figure 6 and a medium density (0.941) PE made in a linear low process.

sequences matching the LLDPE chains which crystallize between 83 and 88°C, then the HP-LDPE chains may cocrystallize with the LLDPE chains at these elevated temperatures (1,2). This is because it is the LLDPE resin whose chains begin to crystallize out first in the TREF fractionation and it is the first component to crystallize out which dictates the structural features to be matched.

The above example represents the most difficult case for separation, because the profiles of the two components overlap almost completely. In the case of a blend of a HP-LDPE and a LLDPE of medium density, TREF allows virtually complete separation (Figure 9). If a large scale preparative-TREF is performed (6) on this blend, the two components can be almost completely separated. This separation allows for a complete and unambiguous determination of the structures of each component of the blend by SEC, NMR, DSC etc.

C. Ethylene-Vinyl Acetates

Ethylene-vinyl acetates prepared by HP processes (HP-EVA) are often blended with polyethylenes to attain improved physical properties. Because they are prepared in a HP process, a homogeneous distribution of the vinyl acetate is expected. However, studies of the TREF behaviour of EVA polymers or blends containing HP-EVA will be complicated because of the presence of short chain branches (C_1 through C_6) derived from the HP process. In order to evaluate the TREF behaviour of EVA containing blends, we have first undertaken to characterize the TREF behaviour of a

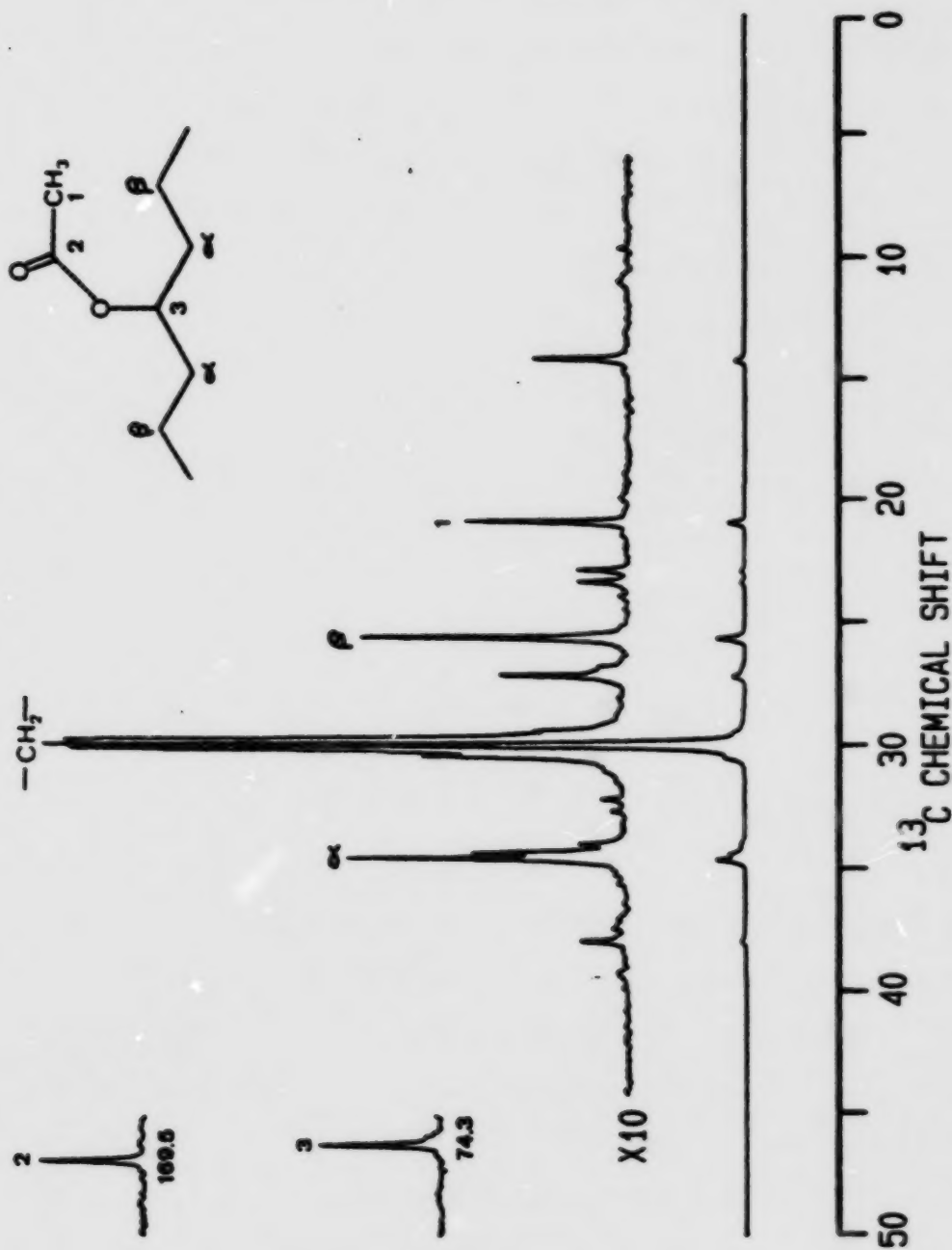


Figure 10.) ^{13}C solution NMR spectrum of EVA-4. The peaks arising from the acetate branches are marked (12) and the remaining peaks can be assigned to alkyl branches (8) generated in the high pressure process used to produce this resin.

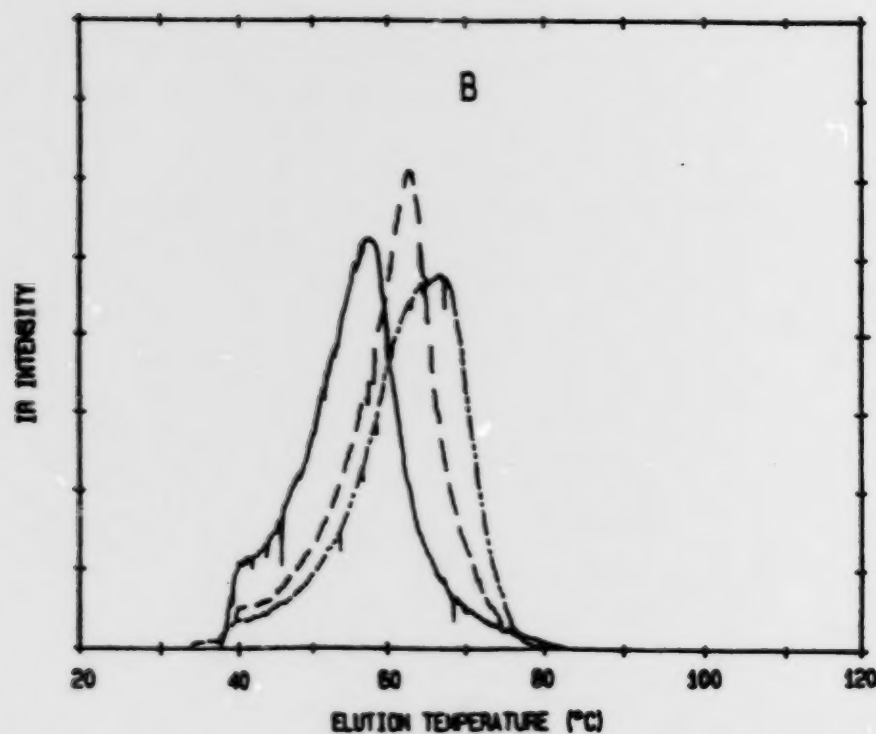
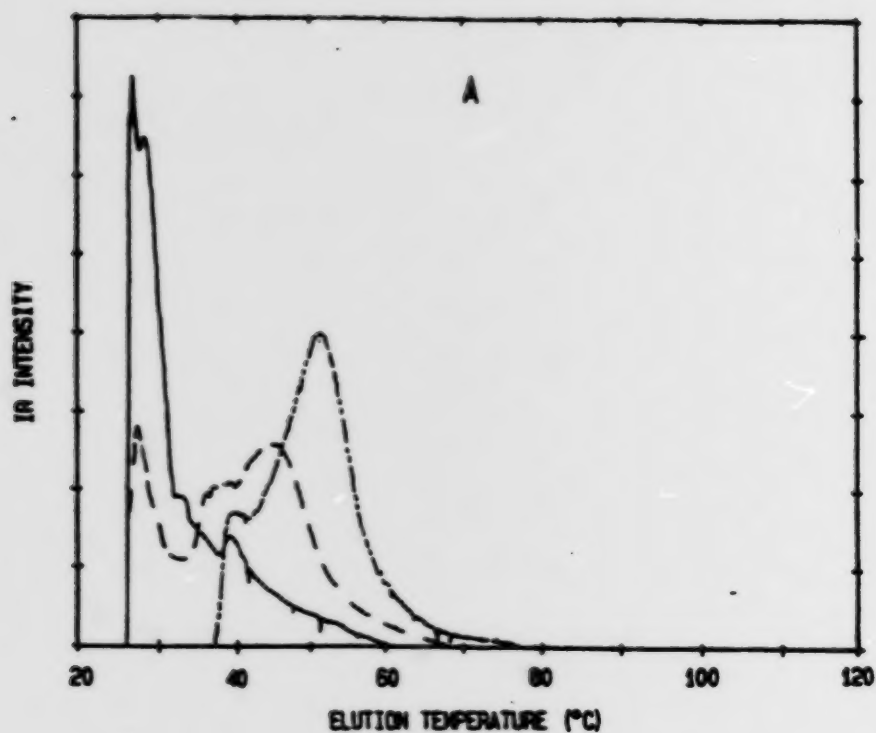


Figure 11.) Analytical-TREF profiles of the six HP-EVA samples examined. See Table 1 for details of the structures. (A) EVA-1 (—), EVA-2 (---) and EVA-3 (-.-) (B) EVA-4 (—), EVA-5 (---) and EVA-6 (-.-).

TABLE 1

Branching Types and Levels in HP-EVA Polymers

Name	Branches/1000 Total Carbons								Wt % EVA by NMR	Mid Temp ¹
	VA	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆ or >	Total		
EVA-1	42.0	-	3.1	-	2.5	0.8	1.7	50.1	23.7	31.0
EVA-2	29.2	-	3.1	-	6.0	2.0	3.5	43.8	16.9	41.5
EVA-3	19.8	0.4	3.2	-	5.9	2.5	5.9	37.7	11.7	51.0
EVA-4	17.5	1.3	3.3	-	6.5	2.0	3.3	33.9	10.4	55.5
EVA-5	12.9	1.4	3.2	0.5	6.5	1.8	3.4	29.7	7.7	61.0
EVA-6	12.9	0.9	2.6	-	5.7	1.9	2.7	26.7	7.7	64.0

1. Analytical-TREF temperature at which 50% of the material eluted.

wide range of EVA polymers. The EVA samples used are commercially produced HP-EVA resins and their branching levels and EVA contents, as measured by ^{13}C NMR, are listed in Table 1.

The ^{13}C spectrum of sample EVA-6 is shown in Figure 10. The presence of a variety of different types of branching is immediately obvious and the assignments of the various types of alkyl branches (8) and acetate branches (12) in the polymers are taken from the literature. Since long chain branches are essentially indistinguishable from C_6 branches, any long chain branching will be included in the C_6 total.

The Analytical-TREF profiles for the 6 EVA polymers are shown in Figure 11. For the polymer with the highest total branching levels (EVA-1), there is a large peak in the TREF at 25°C . This is indicative of material which was still in solution at 25°C and came out of the column immediately upon commencing the elution. As the total comonomer content is increased, the quantity of material which elutes at room temperature decreases and the peak temperature for the elution profile moves to higher temperature. For sample EVA-2, the presence of two peaks in the TREF is deceptive. It may be that the distribution is heterogeneous and gives two peaks, however it is more likely that the peak at room temperature simply represents material which would have eluted at temperatures below 25°C (because of extremely high total branching levels) if the TREF apparatus commenced elution at lower temperatures. For samples EVA-3,4,5,6 there is a clear homogeneous intermolecular SCB distribution, with a strong low temperature tail, similar to that seen for the HP-LDPE resins.

In order to ascertain if the acetate branch has an effect on the elution temperature which is comparable to that of an alkyl branch, the total branching levels of these EVA polymers and the mid temperatures of the elution profiles (the temperature at which 50% of the resin has eluted) have been tabulated in Table 1. In most cases this mid temperature is quite close to the peak in the TREF profile. The EVA data points were then compared to our SCB/elution temperature calibration curve (see Figure 3) which was constructed from narrow fractions taken from an ethylene/butene LLDPE copolymer. The points for the EVA polymers are marked on the graph and they show good agreement with the butene based calibration curve. Since these EVA polymers have a variety of different branches, and since we are taking the mid temperatures of relatively broad profiles rather than narrow fractions, it is not an exact test of the correlation of acetate branches with branches derived from butene. However, the extremely good agreement for all of the samples suggests that to a first approximation, the acetate branches behave like butene branches in the TREF fractionation. A more exact study of this correlation will require narrow fractions, taken from an ethylene/vinyl acetate which was not produced in a HP process, so as to eliminate the complication of the alkyl branches produced in the HP process.

D. EVA/LLDPE Blends

Since the EVA polymers have a distinctive Analytical-TREF profile

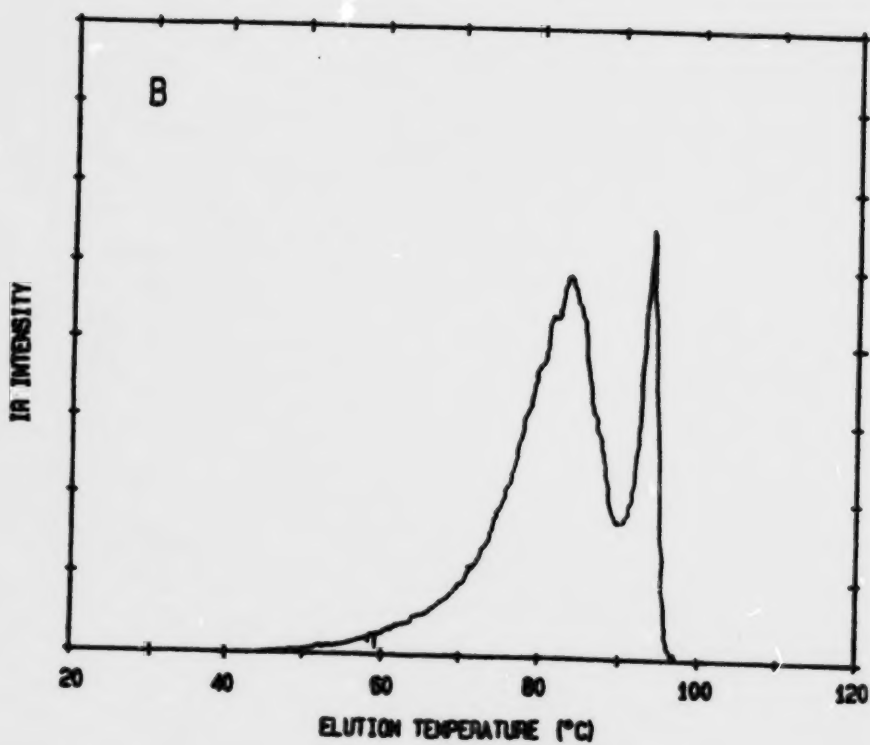
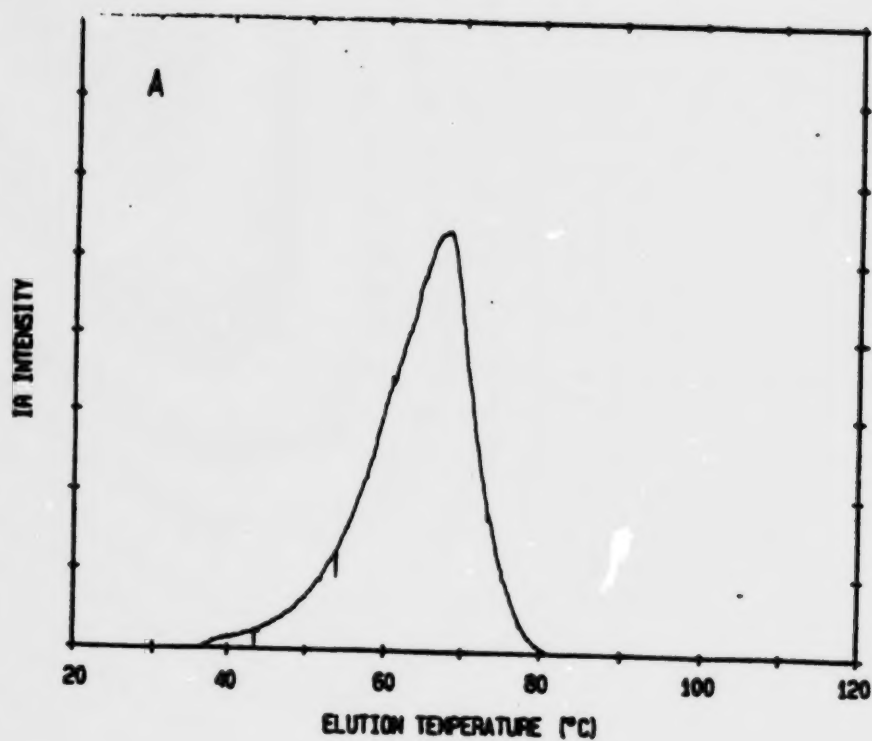


Figure 12.) Analytical-TREF profiles for (A) EVA-6 and (B) an ethylene/octene LLDPE.

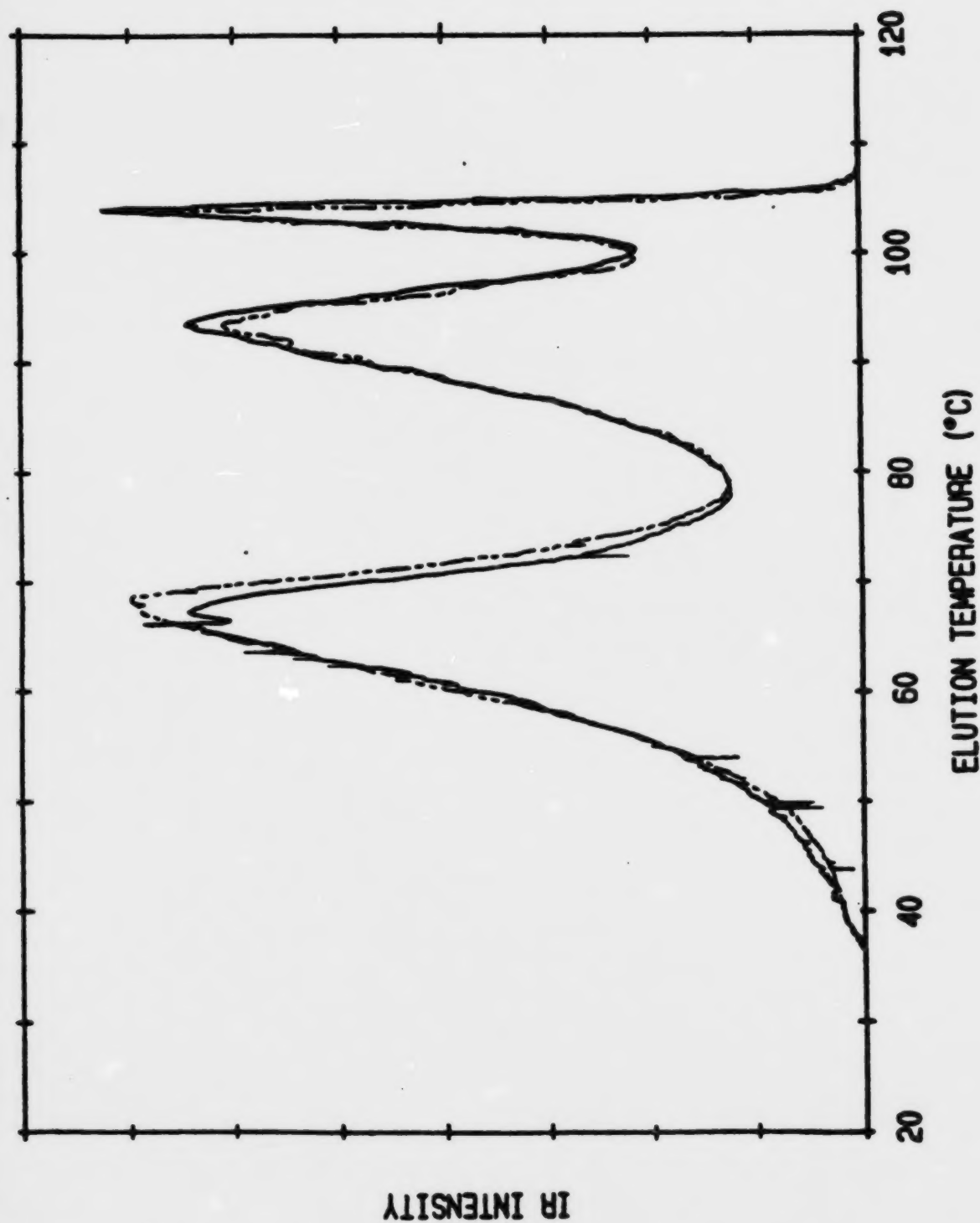


Figure 13.) Analytical-TREF of a 50/50 blend of EVA-6 and the LLDPE shown in Figure 12. Actual blend (—). Predicted blend (---) based on a 50/50 summation of the two TREF profiles in Figure 12.

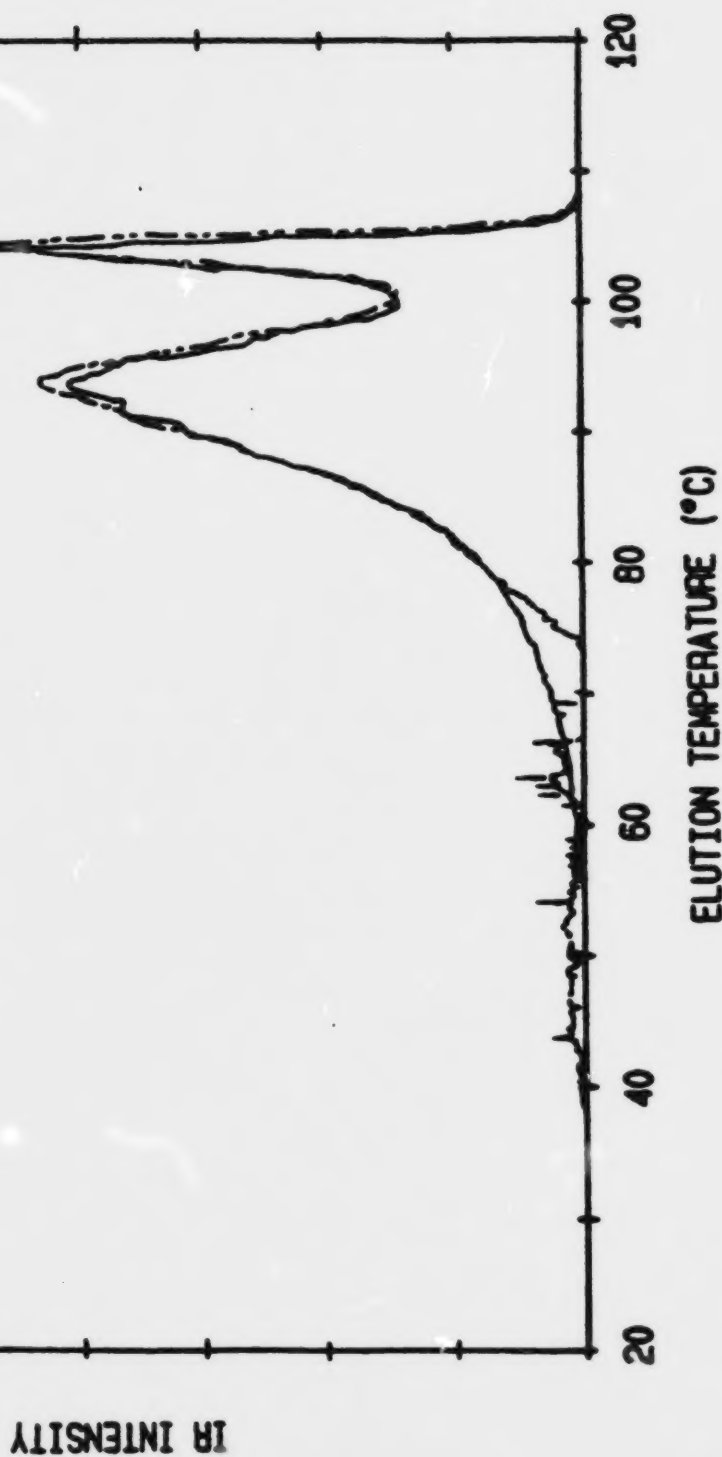


Figure 14.) Analytical-TREF obtained by subtracting the profile of the pure EVA-6 component (shown in Figure 12) from the Analytical-TREF profile of the 50/50 blend (shown in Figure 13). The resulting subtraction (---) shows good agreement with the profile of the pure LLDPE (—).

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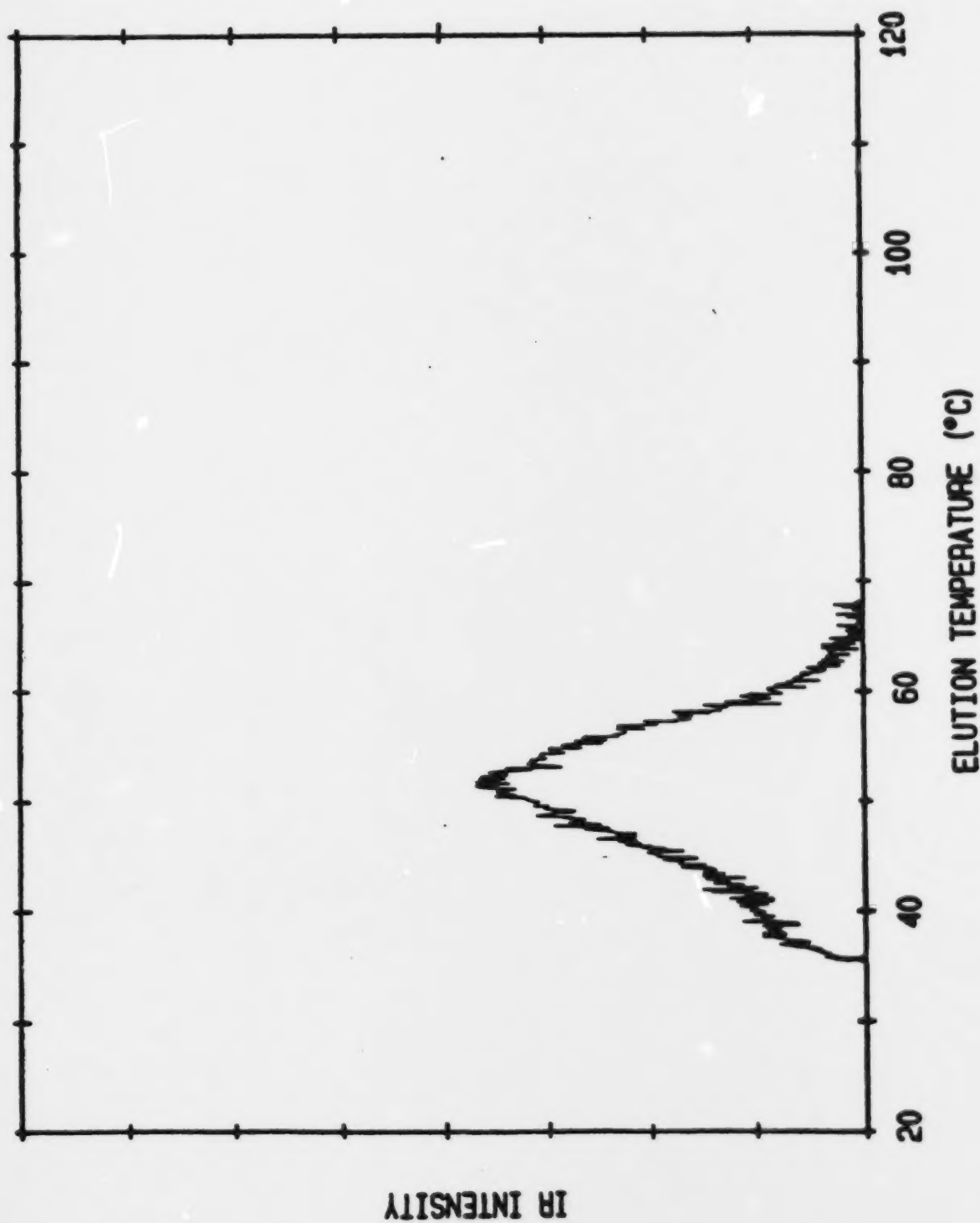


Figure 15.) Analytical-TREF of EVA-3 obtained with IR detection at 1740 cm^{-1} , the frequency of the acetate carbonyl.

relative to LLDPE, blends of HP-EVA and LLDPE are also amenable to study by TREF. Figure 12 shows the Analytical-TREF profiles for an ethylene/octene LLDPE (7.8 branches/1000 total carbons) and the Analytical-TREF for EVA-6. A 50/50 blend of the two polymers gives the TREF shown in Figure 13. The result of a 50/50 summation of the two individual profiles shown in Figure 12 is also included in Figure 13 for comparison. Unlike the HP case, blends of the EVA and LLDPE (at ratios of from 25/75 to 75/25) show better agreement between the actual profile and the summation, suggesting that there is little or no influence of the LLDPE on the crystallization of the HP-EVA as appeared to be the case in the HP-LDPE/LLDPE blends. To confirm this independence of one component from another, subtractions of the pure EVA component from the measured blend result in a LLDPE profile which has excellent agreement with the pure LLDPE polymer (Figure 14).

An alternative route to extracting the EVA component is available if an IR detector is used to record the concentration of the eluting polymer. Figure 15 shows the Analytical-TREF profiles for the pure EVA-3 when detection is done at 1740 cm^{-1} , the IR frequency of the acetate carbonyl. In this TREF experiment, the signal to noise is reduced because of the reduced carbonyl intensity, relative to the C-H intensity. Signal-to-noise also suffers because of the presence of a carbonyl containing antioxidant in the eluting solvent.

Despite the reduced signal-to-noise, the carbonyl derived profile shows good agreement with the C-H based profile, indicating that the acetate branches are distributed throughout the polymer in a similar

manner to the other types of alkyl branches which are observed to be present by NMR. The advantage of this technique is that it enables one to pursue the distribution of non-aliphatic branches or grafts throughout the sample. The only requirement is that the branch or functional group in question have an IR band which is intense and free of interference from the solvent or polyethylene. In blends of EVA and LLDPE, carbonyl detection ensures that only the chains containing acetate branches will be detected by TREF.

E. PE/EPDM and PE/PIB Blends

Since many polyisobutylenes and EPDM terpolymers are soluble in α -chloronaphthalene at temperature below 30°C, TREF can be used to quantitatively separate them from polyethylene. Blends of PIB/PE and EPDM/PE were loaded onto large scale, stop-flow columns at 150°C and allowed to cool slowly to room temperature. The TREF apparatus was reconfigured for stop-flow operation (6) so that material eluting off the column could be collected. The PIB (or EPDM) was collected first by eluting it off the column at 30°C. The PE component can then be eluted off the column, either as an analytical-TREF, or the PE component can be eluted off, precipitated and subjected to SEC and ^{13}C NMR analysis. This TREF based separation is superior to the usual solvent extractions because solvents which take out all of the PIB or EPDM will usually take out highly branched, low molecular weight components of the PE.

CONCLUSIONS

The Analytical-TREF provides an excellent route for characterizing blends based on PE. It is possible to quantitatively characterize a HP-LDPE/LLDPE blend if one knows the shape of the Analytical-TREF profiles of the components which went into the blend. Since the high temperature peak (104°C) of the LLDPE is always clear of the HP-LDPE profile, this makes a particularly good marker for quantifying known blends. In blends containing unknown HP-LDPE and LLDPE components, it is still possible to obtain a good measure of the HP-LDPE/LLDPE ratio if an estimate of the shape of the low temperature portion of the LLDPE profile can be made. Since the overall shape of the low temperature peak of the LLDPE appears to be very sensitive to the process conditions under which they were made (2,3,5) and if the densities are such that the low temperature peak can be resolved from the HP-LDPE, then a reasonable estimate of the HP-LDPE/LLDPE ratio can be achieved using "standard" LLDPE profiles. To increase the probability of success in these estimates, we are attempting to catalogue the shapes of the Analytical-TREF profiles, as a function of method of preparation (assuming a constant density). With this information it should be possible to perform a relatively quick search to identify a most probable Analytical-TREF profile which describes the LLDPE component and use this to subtract from the blend.

The HP-EVA samples appear to behave like HP-LDPE polymers, that is the distribution of the all of the branches appears to be homogeneous. As well, the acetate branches in the polymer appear, to a first

approximation, to have the same influence on the TREF crystallization as the branches introduced by incorporation of a butene. This allows the acetate branching distribution to be studied in the same way as the SCB distribution. Finally, the ability to detect these branches using the carbonyl peak in the IR allows the functional group to be probed independently of other types of branches and suggests possibilities for studying other blends or grafts.

The high branching levels (both alkyl and acetate) in the HP-EVA polymers allow blends of HP-EVA/LLDPE to be well resolved by TREF. When used in conjunction with ^{13}C solution NMR, it is possible to obtain the EVA/LLDPE ratio of the blend, the vinyl acetate content in the HP-EVA, and the type and level of alkyl branching in each of the two components. This represents a considerable improvement over current methods of analysis for EVA/PE blends.

The large scale stop-flow TREF apparatus gives quantitative separations of highly soluble polymers (EPDM, PIB etc.) from polyethylenes. The separations achieved are complete and far superior to those achieved by the usual chemical extractions.

ACKNOWLEDGEMENTS

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ABBREVIATIONS

TREF	- temperature rising elution fractionation
SCB	- short chain branches
PE	- polyethylene
HP-LDPE	- high pressure low density polyethylene
LLDPE	- linear low density polyethylene
EVA	- ethylene-vinyl acetate
EEA	- ethylene-ethyl acrylate
PIB	- polyisobutylene
PP	- polypropylene
EPDM	- ethylene/propylene/hexadiene terpolymer

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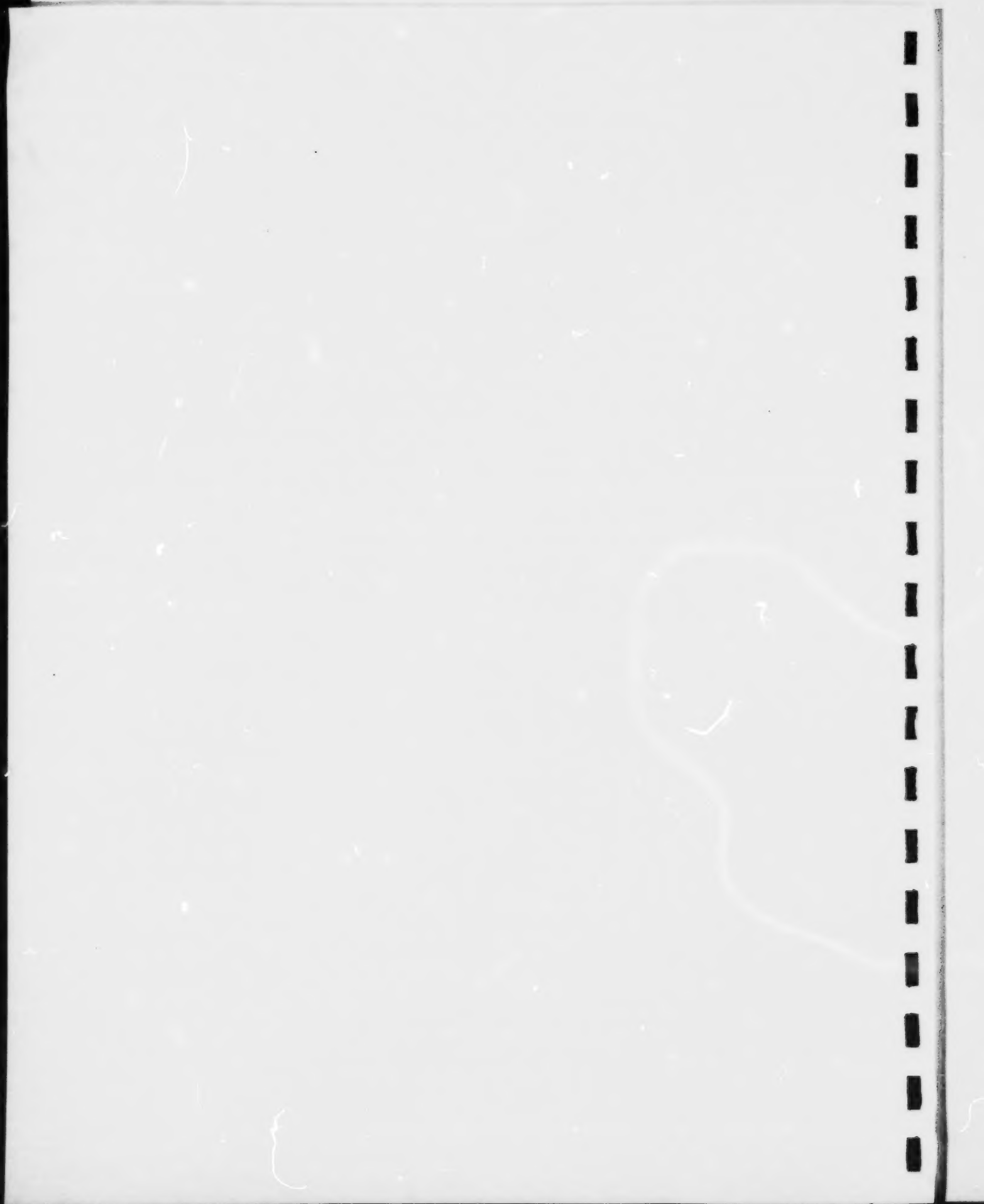
POLYETHYLENE TEREPHTHALATE BLENDS
FOR PERMEABILITY BARRIER APPLICATIONS

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ABSTRACT

Polyethylene terephthalate (PET) offers good properties as a material of choice for various packaging, electronic and other applications. In these applications in general, the PET articles achieve their good toughness and other physical properties by molecular orientation by stretching at temperatures slightly above its T_g . Without such orientation, these suffer from poor impact toughness. We have been investigating modifications of PET for improving toughness and retaining the permeability properties. PET having intrinsic viscosities of 0.5-0.7 have been modified with low modulus polymers, particularly ethylene copolymers such as ethylene-methacrylic acid (EMAA) copolymers. The effect of crystallinity (established by Differential Scanning Calorimetry (DSC) on toughness was determined. Many of these modified polyethylene terephthalate compositions have good toughness and permeability barrier properties for various packaging and other controlled permeability applications such as containers and films.

Polyethylene terephthalate (PET) is widely used in Engineering, Electronic and Packaging applications as injection molded articles, films and containers. A major aspect of PET has been its excellent permeability barrier properties and its elevated temperature performance. While PET itself lacks toughness, molecular orientation above T_g results in imparting excellent toughness and other physical properties. Such operations require physical stretching of the article (such as film or a molded container) in a secondary operation.

The objective here has been to study the modification of polyethylene terephthalate with low modulus polymers to improve its toughness properties without a secondary stretching and orientation process or employing special crystallization techniques, while retaining all or most of its permeability barrier properties.

Experimental

Polyethylene terephthalate of intrinsic viscosities of about 0.5 to 0.7, (measured in 60:40 mixture of phenol and tetrachloroethane) were combined with acid modified ethylene copolymers (4-10% methacrylic acid), zinc and sodium neutralized "ionomers" and other ethylene-vinyl ester (butylacrylate, vinyl acetate, etc) copolymers, in a Werner and Pfleiderer twin screw extruder and injection molded into test articles (flex bars, tensile bars, and containers) or extruded into films. Significant amount of work was also done using Du Pont's recently commercialized "Sclar" PT grades. Toughness properties were determined by notched Izod (ASTM D-256), Gardner impact or instrumented impact testing. Injection molded containers were often tested for impact by dropping filled containers from various heights as well.

The crystallinity of the compositions were measured by a Du Pont 1090 thermal analyzer, analyzing the exotherm (around 120°C) indicating crystallization of the PET. The total crystallinity was determined by the thermal energy absorbed on melting. Usually a 10°C/minute rate was used.

Permeability measurements were made by determining weight losses in a container, filled with the solvent (generally xylene) at room temperature (23°C) or at 60°C. Films were tested for permeabilities by using these as "lids" tightly sealed on top of an aluminum cup. Amorphous specimens were annealed by keeping them in an oven at 120°C until the crystallization peak was not detectable by thermal analysis. Thin crosssections of the extruded strands on the molded article were examined with a transmission microscope to study the polymer blend morphology.

Discussion

Polyethylene terephthalate is widely used as films, containers and injection molded articles. In general the films (e.g. "Mylar") and containers (e.g. carbonated soft drink containers) are stretch oriented, thereby resulting in high toughness and other physical properties. Generally the injection molded articles are crystallized by molding under conditions chosen for crystallization of PET, which involve keeping the mold around 90°C-120°C depending on the compositions. Various technologies are available such as the use of nucleating agents, plasticized combinations, etc. for inducing crystallization. The PET compositions used for injection molding generally are reinforced with inorganic fibers and particulate fillers which also act as nucleating agents. The unreinforced, unoriented PET articles are poor in toughness and are undesirable for most applications.

Our objective was to investigate the permeability properties of PET modified with softer or rubbery polymers to improve toughness, as well as to evaluate these properties as a function of the crystallinity of the PET.

Toughness of PET/Ethylene Copolymer Compositions Where the PET is Crystallized

Extensive studies have been carried out by the author as well as others in developing toughened compositions from PET by combining with low modulus polymers (such as elastomers).

TABLE I

EFFECT OF ETHYLENE-METHACRYLIC ACID COPOLYMERS AND
IONOMERS ON THE TOUGHNESS OF POLYETHYLENE TEREPHTHALATE (PET)

PET	EMAA (10% MAA)	NEUTRALIZATION ION, (%)	% ELONG.	IZOD IMPACT JOULES/METER
100	-	-	<5	13.88
80	20	-	14	27.76
80	20	SODIUM(60)	40	32.02
80	20	ZINC(50)	36	64.05

TABLE II

EFFECT OF ETHYLENE TERPOLYMERS ON THE
TOUGHNESS OF POLYETHYLENE TEREPHTHALATE

PET		POLYMER		TENSILE		FLEX	NOTCHED
VISCOSITY	AMOUNT	TYPE*	AMOUNT	ELONG. %	STRENGTH K.Pa	MOD K.Pa	IZOD JOULES/ METER
1.0	100	-	-				
1.0	80	E/IBA/MAA 78 12 10 72% NEUTR. WITH Zn	20	68	50.33	1792.7	229.5
1.0	70	"	30	160	38.62	1379.0	1233.1
0.7	100	-	-				26.69
0.7	80	E/IBA/MAA 78 12 10 72% NEUTR. WITH Zn	20	13	51.02		90.74
0.7	80	E/VA/GMA 67/28/5	20	170	43.43	1861.7	944.8

*E - Ethylene

IBA - Isobutyl Methacrylate

MAA - Methacrylic acid

VA - Vinyl acetate

Zn - Zinc

GMA - Glycidyl Methacrylate

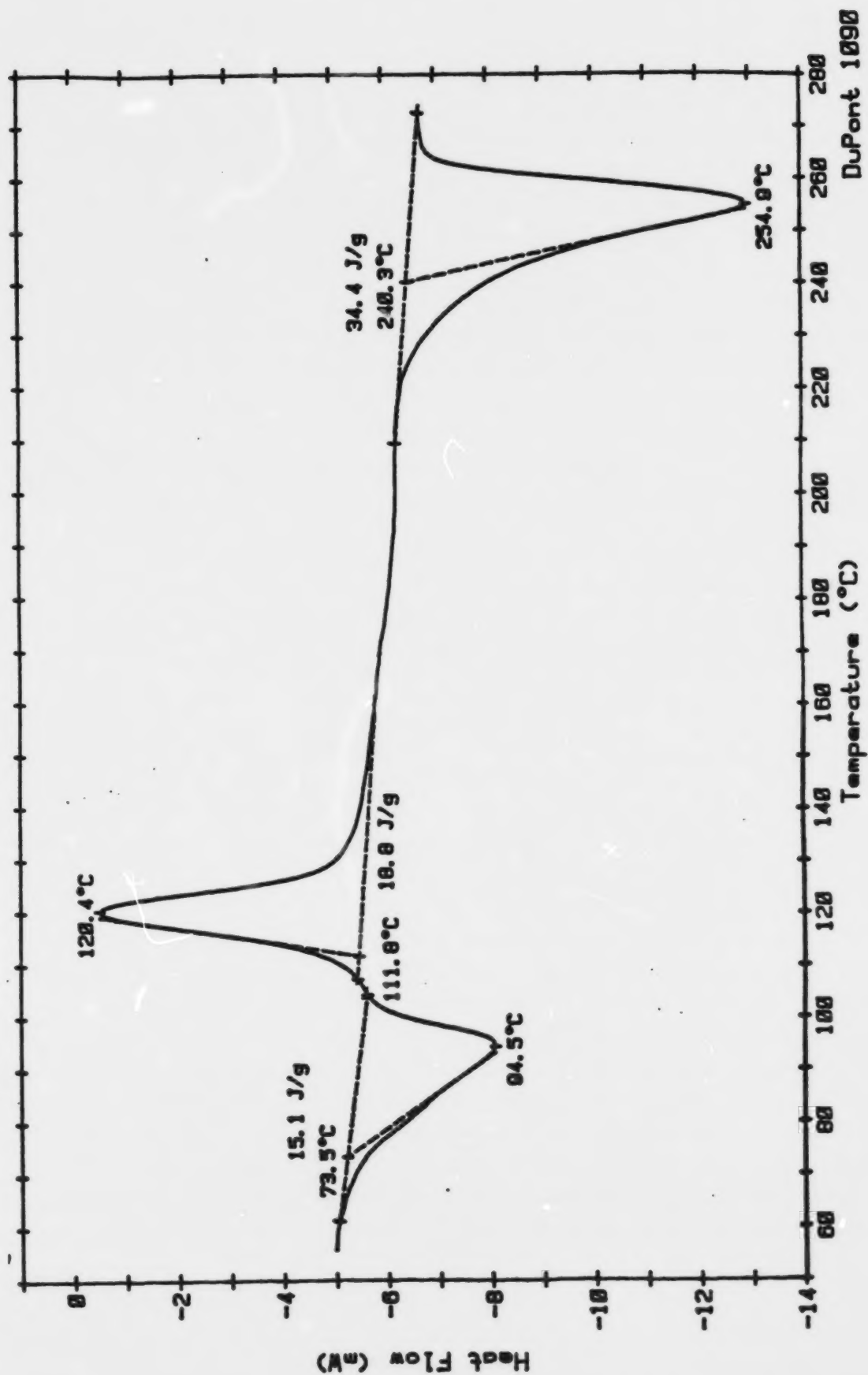


Fig. 1 Thermogram of PET:EMA (80:20) Blend

It was found by Cope(1) that some improvement in the toughness of PET can be achieved by incorporation of ethylene copolymers. The notched izod impact values of the crystallized compositions, showed the least improvement for the composition containing the unneutralized ethylene methacrylic acid (EMAA) copolymer. The use of the sodium salt of the ethylene copolymer resulted in some more improvement and the zinc salt proved to be significantly better as shown in Table I. When the ethylene methacrylic copolymer ionomers contained a termonomer such as isobutyl acrylate, the PET compositions were significantly tougher(2). A significant enhancement of toughness was also found when the molecular weight of PET was increased (Table II).

Effect of Crystallinity on Toughness of PET Compositions Containing Ethylene-Methacrylic Acid Copolymers

The physical properties, particularly impact strength of PET samples described above were obtained after the PET was fully crystallized. The crystallization in those cases were achieved either by post annealing at temperatures up to 200°C or invariably keeping the mold at about 140°C during injection molding of the test specimens.

While high crystallinity is generally required to achieve the ultimate properties, we felt that many applications can tolerate lower amount of crystallinity. Further, very little information was available regarding the toughness properties of less crystalline blends or their permeability properties, which are of great interest to us.

In the following experiments, in order to reduce crystallinity during molding of the articles, the mold temperatures were kept low by using a circulating fluid at about 5°C. Test specimens were cut from the sides of the injection molded article (cup) which had a thickness of 1.14 mm. The crystallinity of these specimens were determined by placing a small piece of the material from the side wall of the container, in a Du Pont thermal analyzer and heating under nitrogen at 10°C/min (Fig. 1). The endotherm at about 95-100°C signifies the melting point of the ethylene-methacrylic acid copolymer. This is followed by an exotherm at approximately 120°C, denoting crystallization of the amorphous sections in the PET. On further heating the

TABLE III

POLYETHYLENE TEREPHTHALATE-ETHYLENE METHACRYLIC ACID COPOLYMER BLENDS (65/35)

TOUGHNESS VS CRYSTALLINITY

MMA	CAT- ION	NEUTRAL- IZATION	AS FOLDED		ANNEALED IMPACT, JOULES	MELTING ENDOTHERM °C	AMORPHOUS CONTENT, %
			CRYSTALLIZATION °C	J/G			EXO/ENDO
4	-	-	117.8	14.4	35.9	194.3	26.9
9	-	-	116.2	13.8	37.06	199.6	29.8
10	Zn ⁺⁺	71	116.5	13.0	37.06	200.1	28.3
10*	Zn ⁺⁺	73	115.3	17.7	37.06	205.6	41.2
10*	Na ⁺	36	111.4	6.4	37.06	218.9	29.9
							53.5
							46.3
							45.9
							43.0
							21.4

*Contains 10% isobutyl acrylate also.

PET melts with the endotherm at around 255°C. The total achievable crystallinity is calculated from this endotherm (or the exotherm when the melted polymer solidifies during the cooling cycle). Figure 1 shows a DSC scan of a blend of PET and EMAA (80/20). In this example the total energy absorbed during melting of the PET amounts to 34.4 Joules/gram (J/g), while the crystallization exotherm has a value of 18.8 J/g indicating that in the specimen 54.6% of the PET remains amorphous.

The impact toughness of these specimens were determined by a "Gardner" drop impact test which measures in Joules (inch-pounds) the force required to break the specimen. Many of these specimens were tested in the "as molded" condition. The impact measurements on the crystallized specimens were carried out after these test specimens were annealed at 120°C for 18 hours (and their complete crystallization established by thermal analysis). The specimens molded under conditions where the PET had not crystallized significantly showed very good impact toughness. Most of the test specimens could not be broken under these test conditions. The differences in toughness between the various samples becomes more apparent when the annealed, crystallized samples are examined (Table III). The zinc neutralized "ionomer" containing PET is tougher than the unneutralized specimens and the ones containing ethylene/isobutyl acrylate/methacrylic acid zinc ionomer is significantly tougher. Even though all specimens are molded under the same conditions, it can be seen that the sodium ionomers containing composition was much less tough. This becomes clear when one examines the crystallinity present in the molded article.

Crystallinity Variations in Molded Articles from PET/Ethylene Copolymers

The crystallinities of the molded articles mentioned earlier are "average". The test specimens were obtained by taking a crosssectional piece and these characterized by thermal analysis. Since the moldings involve use of cooled molds one could visualize a distribution of crystallinity in the wall, the outside and inside sections being more amorphous since they are quenched rapidly and the center being more crystalline. In order to find this distribution, representative samples (inside, center, and outside) were cut from the molded articles and were separately analyzed by Differential Scanning

TABLE IV

INJECTION MOLDED PET BLEND
TUMBLERS - CRYSTALLINITY

ADDITIVE (3%)	CRYSTALLIZATION		PET MELTING		EXO/ENDO	DESCRIPTION OF THE SAMPLE
	°C	J/G	°C	J/G		
E/MAA 96/4	118.9	12.6	254	15.7	0.80	INSIDE
	118.4	11.2	254.2	18.4	0.61	OUTSIDE
	120.4	25.9	253.7	62.1	0.41	MIDDLE
E/MAA (Na ⁺)	103.9	2.58	250.4	10.5	0.24	INSIDE
	101.1	3.75	250.5	21.3	0.18	OUTSIDE
	~100	SMALL	250.9	18.4	~0.01	MIDDLE
E/MAA (Zn ⁺⁺)	119	8.75	253.7	16.2	0.54	INSIDE
	118.6	8.1	254.4	13.3	0.61	OUTSIDE
	115.4	19.2	254.5	47.2	0.41	MIDDLE

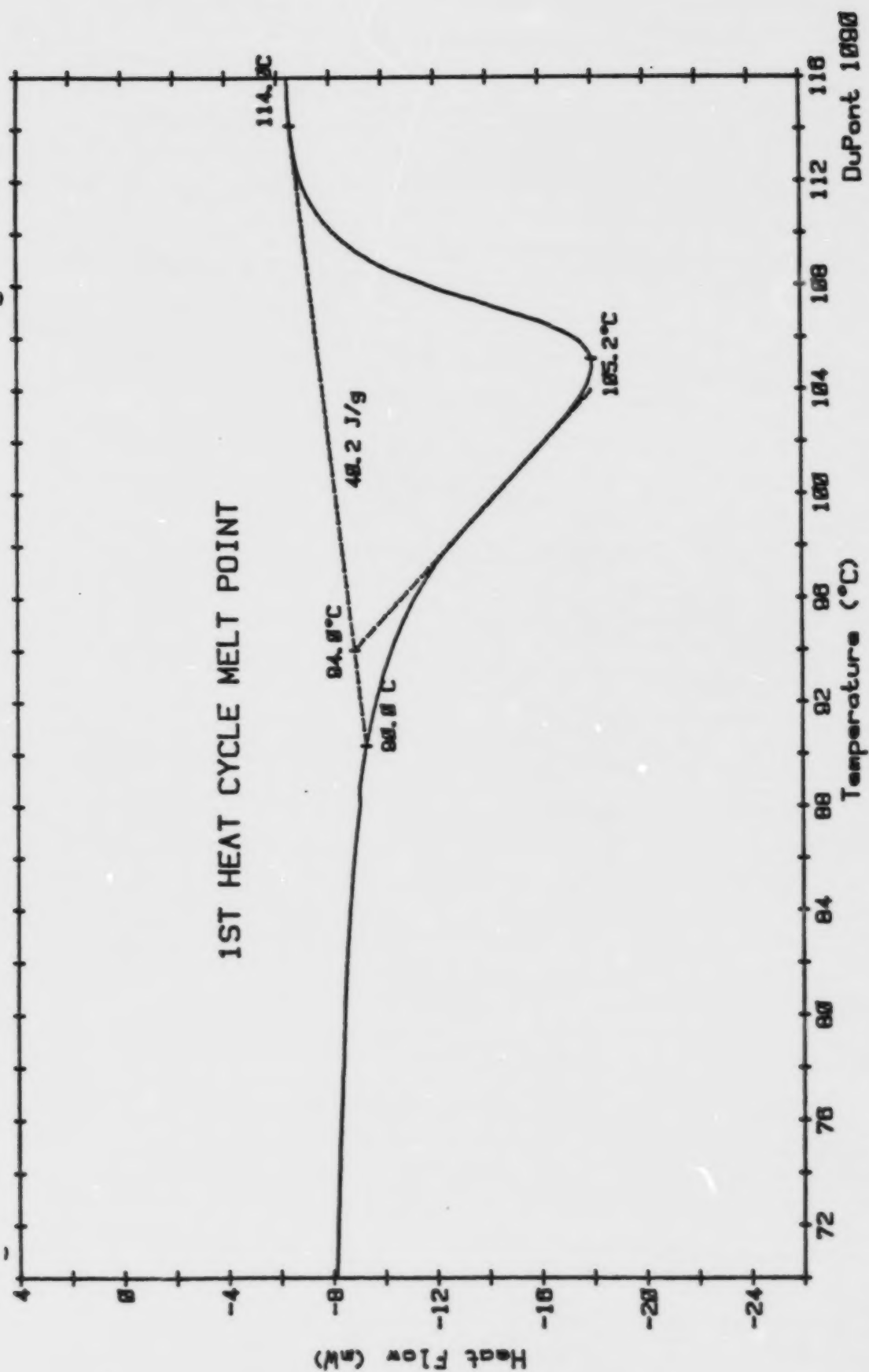
TABLE V

POLYETHYLENE TEREPHTHALATE/ETHYLENE-METHACRYLIC (EMAA) ACID COPOLYMER
(65/35)

XYLENE PERMEABILITY* @ 60°C

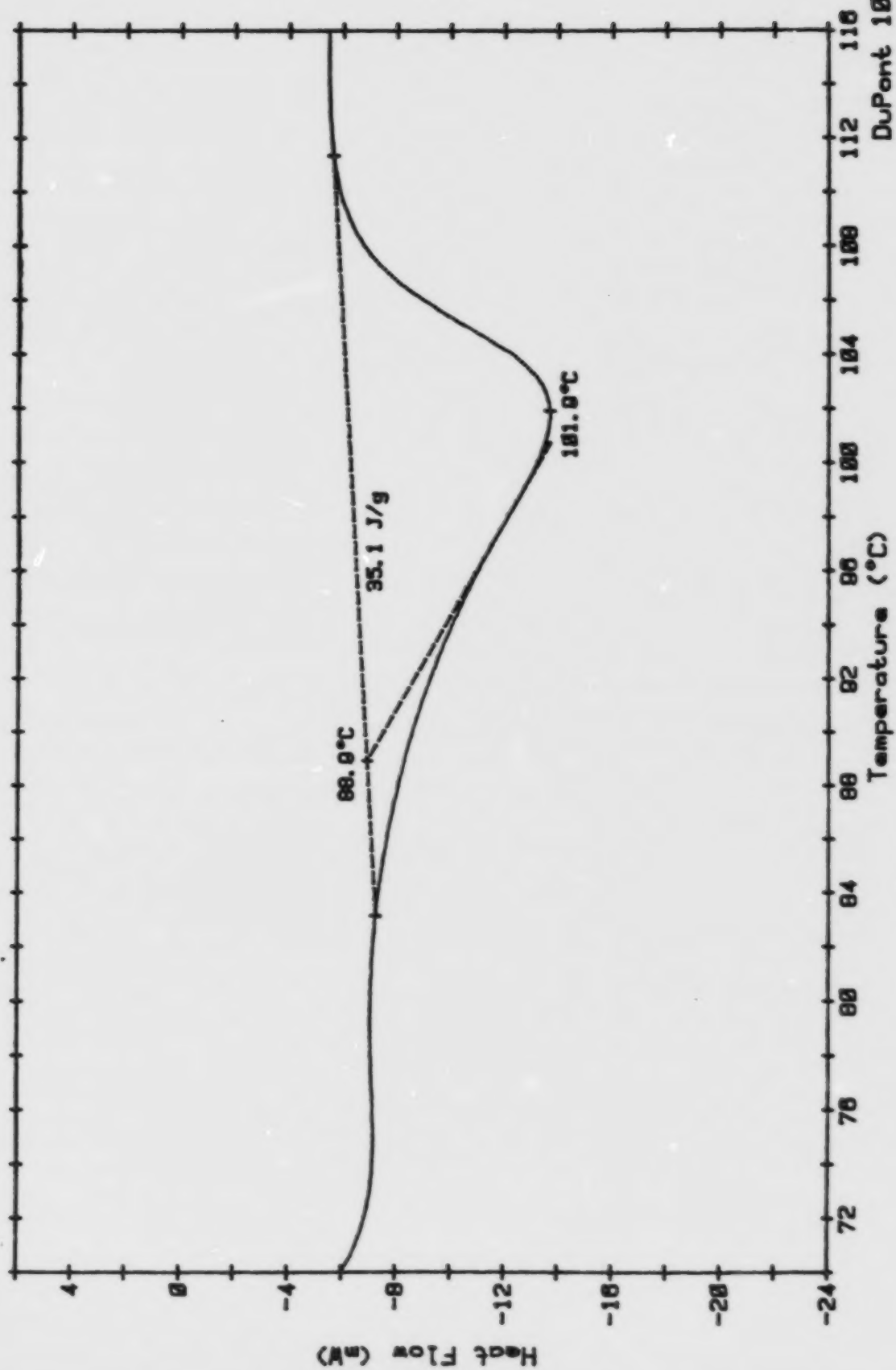
% E	% MAA	IBA	CATION	% NEUTRAL- IZATION	PERMEABILITY LOSS, G/24 HRS
96	4	-	-	-	0.02
91	9	-	-	-	0.08
90	10	-	Zn ⁺⁺	71	0.01
80	10	10	Zn ⁺⁺	75	0.12
80	10	10	Na ⁺	36	0.04

*INJECTION MOLDED TUMBLERS .045 IN. THICK "2" DIA.
TESTED FOR 688 HOURS.



9/12

Fig. 2 Thermogram of EMAA (48 MAA)



9/13

Fig. 3 Thermogram of EMAA (91 MAA)

TABLE VI

SOLVENT BARRIER OF "SELAR" PT AT 40°C

SOLVENT	PERMEATION ($\frac{\text{gm}}{\text{mm}^2 \cdot \text{day}}$ at 1 atm)
XYLENE	0.39
10% METHANOL/90% XYLENE	0.24
15% ACETONE/XYLENE	0.75
ACETONE	5.5
METHYLETHYL KETONE	<0.16
ETHYL ACETATE	<0.16
1,1,1 TRICHLOROETHANE	0.43
TRICHLOROETHYLENE	16
PAINT-SOLVENT BASE	0.3-.5
VARNISH	0.55
SHELLAC	0.35
HDPE (XYLENE)	58.5

(TESTS PERFORMED ON 118 ml "SELAR" PT INJECTION BLOW MOLDED BOTTLES.)

Calorimetry (DSC). Table IV gives the information from the DSC on the separate sections. Included are information on the sections from articles molded from PET containing EMAA copolymer, a zinc ionomer and a sodium ionomer. In the case of the specimen containing unneutralized ethylene-methacrylic acid copolymer as well as the zinc salt, the outside and inside layers are substantially amorphous, while the middle layer is significantly more crystalline. When the sodium salt of ethylene-methacrylic acid copolymer was used, the crystallinity is more uniform throughout and much higher than in the other cases. The nucleating effect of the Na^+ ions is shown by the higher crystallinity of the PET in this specimen even though the molding was carried out under similar conditions (the mold temperature about 5-10°C).

Of particular interest, besides toughness, are the permeabilities of the articles from these modified compositions. Xylene permeabilities determined in injection molded containers are given in Table V. On examination of these permeabilities (as determined by weight loss), some trends appear clearly. Among compositions containing ethylene-methacrylic acid copolymers, the higher acid (9%) containing compositions is more permeable. This can be explained by the lower crystallinity of the higher methacrylic acid containing copolymer (Fig. 2,3). The ionomers are somewhat better. In general these are substantially less permeable than polyolefins even though the PET in these containers have not been fully crystallized.

Additional modifications have resulted in the development of a series of "barrier" resins for injection molding, injection blow molding and extrusion purposes by Du Pont (as "Selar" PT). Typical permeability barrier properties of one of these compositions are given in Table VI. These resins, besides having excellent solvent barrier properties, have shown outstanding toughness properties as demonstrated by drop testing at low temperatures.

Morphology of the PET/Ethylene Copolymer Blends

The dispersion of the ethylene copolymers within the PET has a profound effect on the toughness and permeability properties. In order to examine the dispersion of the ethylene copolymers, thin specimens from the

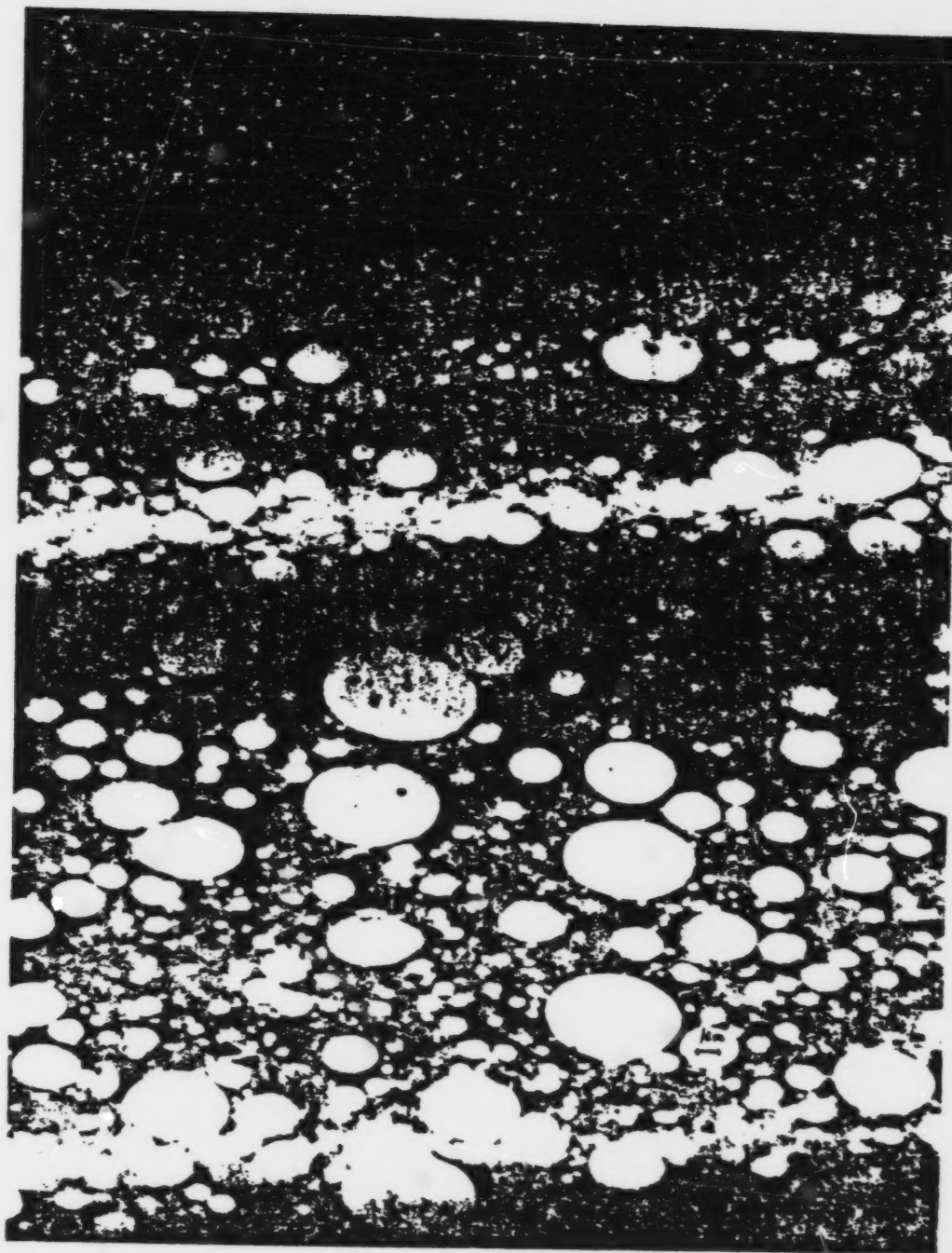


Fig. 4

Photomicrograph of PET:EMAA (4% MMA) (perpendicular to flow)



Fig. 5

Photomicrograph of PET:EMAA (4%)
(parallel to flow)

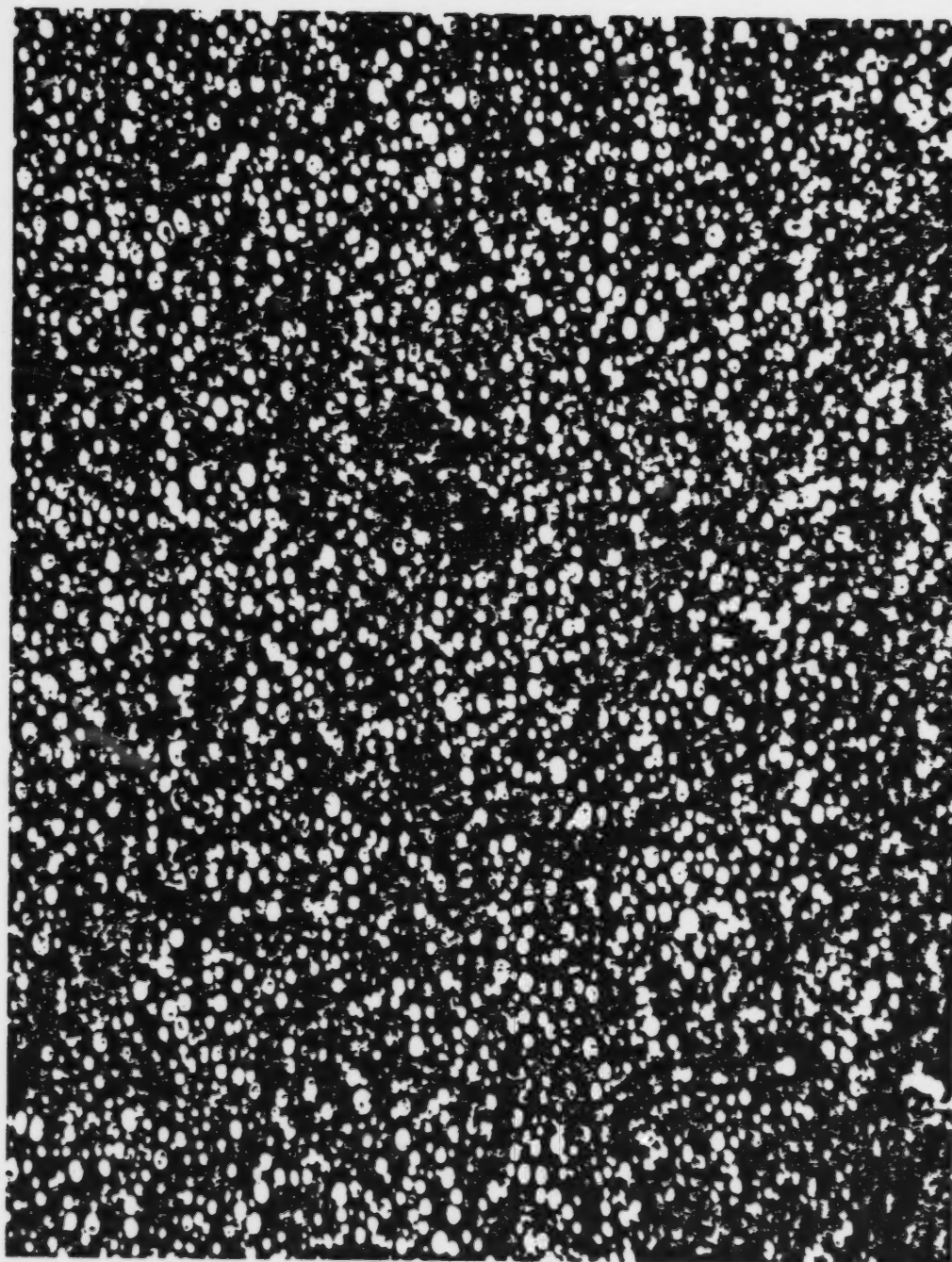


Fig. 6

Photomicrograph of PET:EMAA (9% MAA)

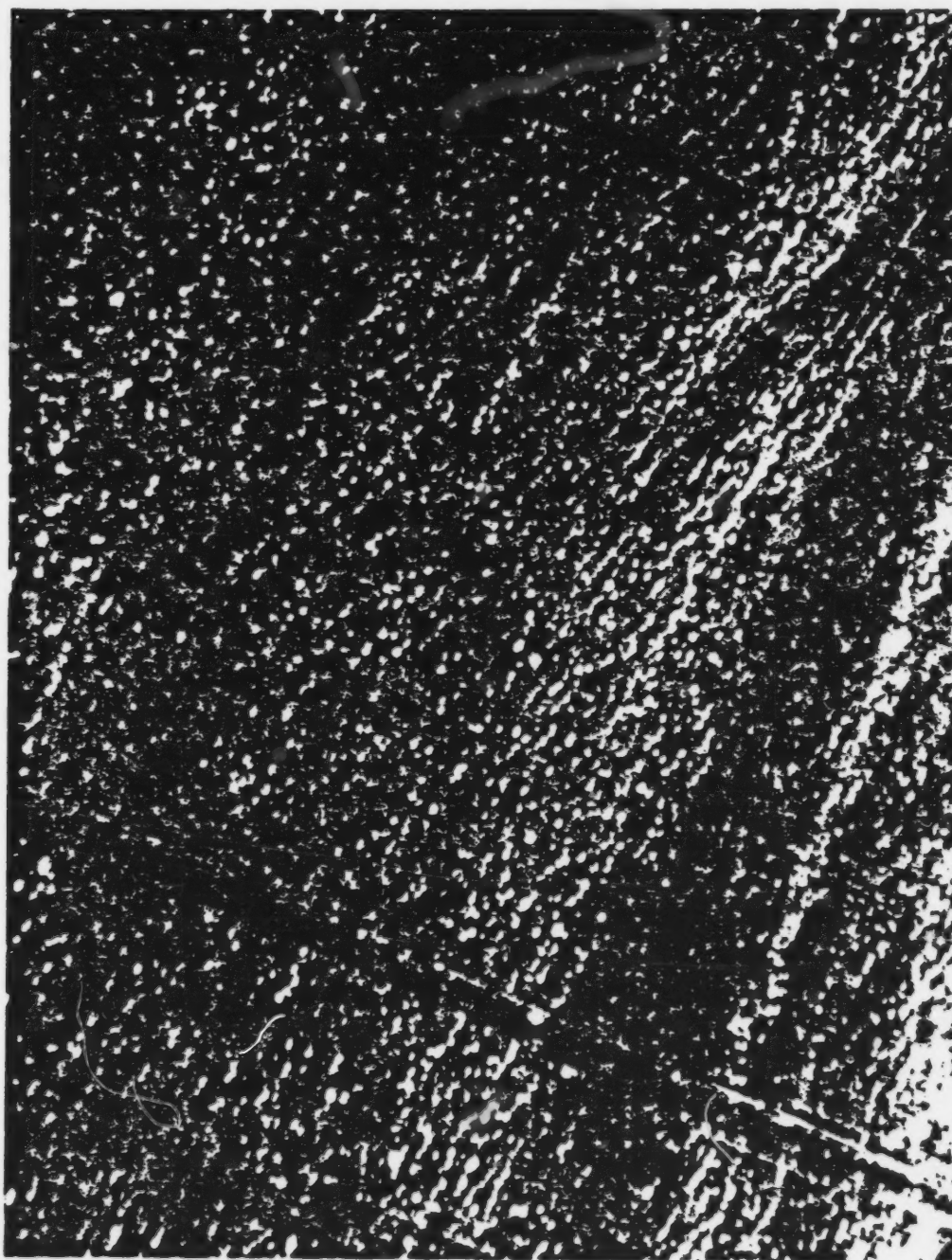


Fig. 7

Photomicrograph of PET:E/TBA/MAA zinc ionomer

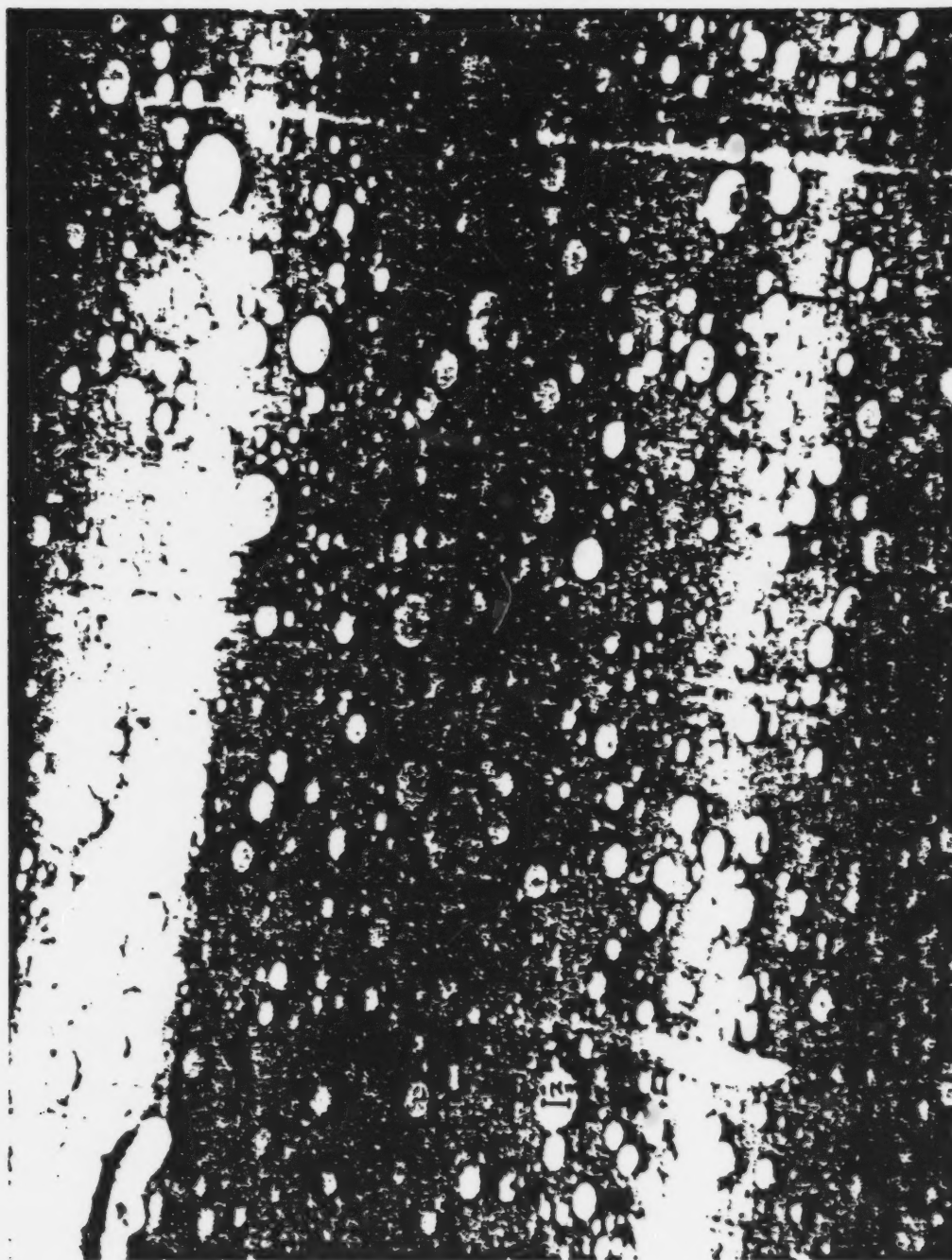


Fig. 8

Photomicrograph of PET:E/IBA/MAA sodium ionomer

extruded or molded article were microtomed and examined under a transmission microscope at various magnifications. Fig. 4 shows the dispersion of EMAA with 4% methacrylic acid in PET. The EMAA particles are large. The same specimen, when examined in the flow direction (Fig. 5) reveals the large elongated particles of the ethylene copolymer. This poor dispersion explains the reason why these blends have lower impact toughness. The 9% methacrylic acid containing ethylene copolymer disperses into much smaller particles (Fig. 6). When one views the ionomer blends similar variations can be seen. The ethylene-isobutylacrylate-methacrylic acid copolymer - zinc ionomer disperses into very fine particles, reflecting the high toughness of these blends (Fig. 7). This is contrast to the large particles of the sodium ionomer and the resulting weaker impact properties (Fig. 8).

Conclusion

Polyethylene terephthalate blends with ethylene-methacrylic acid copolymers and some of their zinc and sodium salts show high toughness properties. The zinc ionomers are more effective than the unneutralized polymers. The amount of crystallinity has a significant effect on the toughness of the articles as well. These modified PET compositions offer good permeability barrier properties for hydrocarbons and other organic solvents.

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POLYMER BLENDS, THEIR PREPARATION, PROCESSING, AND ECONOMIC FORECAST

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SYNOPSIS

The plastics industry shows the highest growth rate of all industrial materials. Within this group the polymer blends are developing fastest. The commodity resin blends (viz. polyethylene or polyvinylchloride) already dominate the market, while the new, multifunctional engineering resin blends expanded to about 20% engineering resin production. Each year there are 4,500 new patents on polymer blends out of which over 1,000 deals with the high performance materials.

The commercial polymer blends are manufactured in two stages: compounding and forming. Most of compounding is done by resin manufacturer (65%), some by companies specializing in compounding (25%) and the remaining 10% by processors. The main goal of compounding is stabilization of morphology i.e. generation of desired reproducible, properties. The alloying uses several methods of compatibilization. Only for the 10% of blends prepared by processors the stabilization step may be omitted. In principle the well compounded alloys can be processed on standard equipment. However, due to strong effects of temperature and pressure on polymer miscibility a significant know-how is required to optimize the process. Another complication may originate in shear flow segregation leading to weak, pinchlines, weldlines and seams as well as to swirls and layering. Here again the knowledge of blend flow behavior is crucial in solving the problem. The motto for the plastics industry is "learn or perish".

INTRODUCTION

In 1985, US sales of plastics exceeded 20 million metric tons out of which about 8% was the contribution from the five principal engineering resins (ER): nylons (PA), polycarbonates (PC), polyphenylene ethers (PPE), acetals (POM) and thermoplastic polyesters (TPE) [1,2]. These numbers may give a wrong impression; already in 1985 the value of ER constituted 14% of the total, and with the expected continuously higher growth rate of these high performance materials (1985 annual growth rate of plastics was about 4%, of ER about 8%) their relative importance will dominate the industry.

Financial balance aside it has to be recognized that ER has contributed enormously to the advancement of science and technology. Without the five "workhorse" ER's progress in transport, business machines, electrical, electronic or appliance industries would be hard to imagine. Without these and the newer high performance resins, e.g. aromatic polyamides, polyimides, polyetherimides, etc., much state-of-the-art technology in wide-ranging fields would simply not be possible.

The tendency toward, on the one hand, high performance engineering materials and on the other toward specialty grades of commodity polymers will continue to intensify. As an example, the rating for 200°C continuous use of high heat grades of polyether imides has already been approved. Within a year or two polybiphenylenesulfides with UL350C are expected to reach the market [3]. Parallel with these heat stability improvements, are advances in mechanical properties, especially modulus, flexural strength and impact

resistance [4].

In commodity resins polypropylene with controlled rheology, crosslinkable polyethylenes, linear low density polyethylene with tailored molecular structure via reactive processing, solid state formed polyolefins, all indicate rapid increase of technical input into polymer technology [5].

Experience shows that development of a new polymer from concept to pilot scale takes 10 to 15 years at a cost of 10 to 50 million dollars without any guarantee of commercial success [6]. Construction of a manufacturing plant requires an additional 40 to 100 million dollars [7]. Both time and cost are very much against development of new, especially commodity type, resins.

Extrapolating from the present trends one can expect [8-11]:

- (i) no introduction of a new chemical-type polymer into the commodity market;
- (ii) the chemistry will play a role in engineering and specialty resins as well as in modification of commodity polymers;
- (iii) use of polymer blends and alloys will dominate the thermoplastic market in both commodity (especially linear low density polyethylene, LLDPE, and polyvinyl chloride, PVC) and engineering resin applications;
- (iv) advances in processing and process control will allow to optimization of morphology, generating desired anisotropic properties and/or

Table 1. DEFINITIONS

POLYMER BLENDS (PB):	Mixtures of chemically different polymers and/or copolymers.
POLYMER ALLOYS (PA):	Polymer Blends with modified interfacial properties and/or morphology.
MISCIBLE PB:	PB behaving as a single-phase system down to molecular level of dispersion, usually associated with $\Delta H_m < 0$.
COMPATIBLE PB:	Utilitarian term indicating commercially attractive PAB; usually system homogenous to the eye with enhanced physical properties.
COMPATIBILIZATION:	Any physical or chemical action which results in stabilization (prevention to separate) of PB.
ENGINEERING POLYMER: (EP)	Processable polymeric material, capable of being formed to precise and stable dimensions, exhibiting high mechanical properties at continuous use at temperature above 100°C and having the tensile strength in excess of 40MPa (6kpsi).
ENGINEERING PB (EPB)	: PA or PB exhibiting properties and/or containing EP as at least one component of the blend.

controlling the limiting factors of the present day operations (viz. weld or pinch lines, melt fracture, etc.).

POLYMER ALLOYS AND BLENDS

To avoid confusion the terms are defined in Table 1. Currently, polymer alloys and blends (PAB), constitute 16% of plastics consumption. The average growth rate of PAB is twice as high as that of all plastics and, for high performance engineering PAB, three times as high [12].

There are a number of reasons for blending [9,10,13-15]:

- a) Generation of unique material as far as its processability and/or performance are concerned;
- b) Extending the performance of expensive resins;
- c) Quick modification of performance;
- d) Higher performance at a reasonable price;
- e) Reuse of plastics scrap;

PAB are frequently divided into two main groups: (i) engineering blends at >\$4/kg and annual growth rate of 16%, and (ii) the commodity resin blends at about \$1.5/kg and a growth rate of 12%. The reasons (a)-(c) are pertinent to the engineering blends, (b)-(d) to the commodity resin blends. Reuse (e) is a volatile subject. It depends on the national policy and to a large extent on the world price for oil. Reuse is important for both groups of polymer blends.

Table 2. CLASSIFICATION OF PAB BASED ON MISCIBILITY

- I. MISCIBLE BLENDS: Behaving as a homopolymer with properties determined by composition. Example: polyphenylenether (PPE)/polystyrene.
- II. IMMISCIBLE BLENDS: Mechanical mixture of two immiscible polymers whose properties depend primarily on the type of processing and on process parameters. Commercially attractive materials can be generated usually via careful control of morphology. Example: polyethyleneterephthalate (PET)/polyamide-6,6 (PA-6,6) blends for monofilament application, "modified" or "toughened" ER containing 2 to 4% of polyolefin or rubber.
- III. COMPATIBILIZED BLENDS: Immiscible blends with modified interfacial properties. In most cases modification involves addition of an agent which interacts with both phases, viz. block or graft copolymer, ionomer, co-solubilizer etc. Example: PPO/polyethylene/styrene-ethylene-butylene block copolymer (SEBS).
- IV. BLOCK POLYMERS AND THEIR BLENDS: This is a more recent class of materials made up of macro-segments of different nature. Example: linear polyurethanes (PU), polyetherimides (PEI), polyether-block-amide (PEBAX), etc. Depending on the chemical nature of macro-segments a wide range of properties can be obtained. In addition these polymers are particularly interesting for use in blends.

Another way to divide the subject is to consider their miscibility. The list is given in Table 2. In reality, the sharp division does not exist. For example, addition of a compatibilizer may affect the final properties not only by improvement of mechanical performance but also by decreasing the weatherability or solvent resistance. A compromise is usually required. A certain amount of peeling and streaking in injection molding (typical for non-miscible blends) may have to be tolerated.

Alloying polymer blends involves many operations, leading to stable and reproducible properties. Alloying may provide stabilization of the interphase by addition of a compatibilizer, just as surfactant stabilizes an emulsion, but this may be done equally well through a chemical reaction or by high shear mechanical re-entanglement.

At present, alloying is a more common practice than it appears in the statistics; a large percentage of "new" commodity resins announced each year are in fact standard grades modified by blending in a polymeric additive. Blending of homologous resins is a common practice in the polyalkenes industry. Blending of LLDPE is particularly common. Blends with LDPE, PP, rubbers are described in the literature [16-23]. Blending LLDPE with PP seems to be particularly interesting for future development.

ENGINEERING POLYMER BLENDS (EPB)

During the last few years, the progress in engineering PAB was

Table 3. COMMERCIAL EPB (1985)

No.	Polyblend	Producer	Composition
1.	Alphalon	Custom M.P.	Elast./PTFE
2.	Alton	Intl. Polym. Corp.	PPS/PTFE
3.	Arloy	Arco	PC/SMA
4.	Arylon	US Steel	ABS/PSF
5.	Bayblend	Mobay	PC/ABS
6.	Bexloy C,J,V or W	Du Pont	PA,PBT,TPE or ionomer/Elast.
7.	BR	Phillips	PPS/PTFE
8.	Cadon	Monsanto	ABS/SMA
9.	Celcon	Celanese	POM/Copolymer
10.	Celanex	Celanese	PBT/PET
11.	Cycoloy	Borg-Warner	ABS/PC
12.	Cycovin	Borg-Warner	ABS/PVC
13.	Delrin	Du Pont	POM/Elast. or PTFE
14.	Duralloy	Celanese	PBT or POM cop./PU-Elast.
15.	Dynyl	Rhone Poulenc	PA/PA
16.	Elemid	Borg-Warner	ABS/PA
17.	Formaldafil	Wison-Fiberfil	POM/PTFE
18.	Gafite/Gaftuf	GAF	PBT/Elast.
19.	Geloy	General Electric	ASA/PVC or PMMA
20.	Grilon	Emser	PA/Elast.
21.	GX-200	General Electric	ASA/PC
22.	Kralastic	Uniroyal	ABS/PVC
23.	Lauranyl	BASF	PPE/TP
24.	Lexan	General Electric	PC/PE
25.	Lustran	Monsanto	ABS/SAN or PVC/SAN
26.	Makroblend	Mobay	PC/PET/Elast.
27.	Merlon	Mobay	PC/PE
28.	Mindel	Union Carbide	PSF/ABS or PET
29.	N5	Thermofil Inc.	PA/ABS
30.	Noryl	General Electric	PPO/HIPS
31.	Noryl-GTX	General Electric	PPO/PA
32.	Nycoa	Nylon Corp.	PA/Ionomer or P01.
33.	Nydur	Mobay	PA/Elast.
34.	Oxytuf	Occidental Chem.	PVC/EPDM
35.	Pebax	Rhone Poulenc	PEth/PA
36.	Pocan-S	Mobay	PBT/Elast.
37.	Polycomp	LNP	PPS or PET/PTFE
38.	Polyman	Schulman	PVC/ABS
39.	Prevex	Borg-Warner	PPE/HIPS
40.	Proloy	Borg-Warner	ABS/PC
41.	Pulse	Dow	PC/ABS
42.	Rimplast	LNP	PA-6,6/Silicone
43.	Ropet	Rohm and Haas	PET/PMMA

Table 3. COMMERCIAL EPB (1985) (cont.)

No.	Polyblend	Producer	Composition
44.	Royalite	Uniroyal	PC/ABS
45.	Rynite SST	Du Pont	PET/Elast.
46.	Selar	Du Pont	PA/POL.
47.	Terblend-S	Badische	ASA/PC
48.	Texin	Mobay	PU/PC
49.	Thermalloy	CdF Chimie	ABS/
50.	Thermocomp	LNP	ABS or POM/PTFE
51.	Ultem	General Electric	PEI/TP
52.	UP	Unitika	PAr/PET
53.	Valox	General Electric	PBT/PET or PC
54.	Vectra	Celanese	LCP Blends
55.	Vythene	Alpha Chem. Plast.	PVC/PU
56.	Xenoy	General Electric	PC/PBT or PET
57.	Zytel	Du Pont	PA/POI, EPDM or Ionomer
58.	-	Albany Intl. Res. Co.	PEEK/PEI

Table 4. AUTOMOTIVE PLASTICSEngineering Resins to Replace SMC and RIM [26]

MATERIAL	COMPOSITION	MANUFACTURER
Noryl-GTX	nylon/PPE alloy	General Electric
Lomod	polyester elastomer	General Electric
Bexloy	modified amorphous nylon	DuPont
-	modified nylons, PBT and polycarbonate	Mobay Chemical
Elemid	nylon/ABS	Borg-Warner
Proloy	polycarbonate/ABS	Borg-Warner
XBR-2-1	PBT blend	Celanese
Arimax 1000	-	Ashland
Caprim	nylon-6 RIM system	Allied
Nyrim	nylon RIM	Monsanto/DSM
-	Polydicyclopentadiene RIM	Hercules

Claimed Advantages:

- On-line paintability,
- Toughness and stiffness,
- Chemical resistance,
- Color consistency,
- Manufacturing economics,
- Low finished part cost.

Use of Plastic in 1990 Cars

Wheels	Headlight lenses
Bumpers	Seat frames
Body panels	Driveshafts
Fron end	Under-hood parts
Leaf springs	Chassis
Fuel tanks	Disc brakes
Windshield coatings	

Table 5. NEWER ENGINEERING AND/OR SPECIALTY RESINS OR THEIR BLENDS

No.	Developing Resin	Suppliers	Competing Resins	End-Use Markets
1.	POLYARYLATE (PAr)	Unitika Union Carbide Solvay Bayer Hooker	Polycarbonate Polysulfone PBT/PET	Appliance Industrial Transportation Electrical/ Electronic
2.	POLYETHER-SULFONE (PES)	ICI BASF	Polysulfone Polyamideimide Polyphenylene sulfide	Transportation Electrical/ Electronic Medical
3.	STYRENE-MALEIC ANHYDRIDE (SMA)	Arco Monsanto Dow	ABS Polyphenylene oxide/styrene	Appliance Transportation Business machines
4.	POLYESTER-POLYCARBONATE (PEC)	Allied Mitsubishi	Polycarbonate Polyarylate	Appliance Industrial Transportation Electrical/ Electronic
5.	POLYIMIDES (thermoplastic) (PI)	Rhone-Poulenc Upjohn	Polyamideimide Polyimide (thermosetting)	Industrial Electrical Aircraft
6.	POLYAMIDE ELASTOMERS	ATO Chimie Emser Werke Huels	Copolyester elastomer Thermoplastic polyurethane	Transportation Machinery
7.	POLYAMIDEIMIDE (PAI)	Amoco	Polyimide Polyphenylene sulfide	Industrial Machinery
8.	POLYESTER ELASTOMERS	DuPont Akzo-Toyobo	Synthetic elastomers	Industrial Automotive
9.	POLYETHERKETONE (PEEK)	ICI	Polysulfone Polyimide PPO	Electronic Medical Chemical Aerospace

Table 5. NEWER ENGINEERING AND/OR SPECIALTY RESINS OR THEIR BLENDS (cont.)

No.	Developing Resin	Suppliers	Competing Resins	End-Use Markets
10.	POLYETHERIMIDE (PEI)	General Electric	Polycarbonate ABS, PPO	Aerospace Automotive Electrical Appliances
11.	POLYETHER-BLOCK-AMIDE (PEBAX)	Atochem	Polyamide ABS, PPO Polyesters	Automobile Business Machines Electrical Recreational
12.	LIQUID CRYSTAL POLYMERS (LCP)	Dartco Celanese	Thermosets Polyphenylsul- fide	Automotive Outdoor uses Oil field Electrical/ Electronic Aerospace
13.	POLYARYLETHET (PAE)	Union Carbide	Polysulfone	Structural Aerospace Electrical
14.	POLYIMIDE SULFONE (PIS)	Celanese (NASA)	Polycarbonate Polysulfone PPO, Polyimide	Electrical/ Electronic Transport Industrial

particularly impressive. These materials, developed with significant proprietary R&D efforts, are shrouded in a cloak of confidentiality by the manufacturers and frequently by the users. Their production in the US during 1983 was estimated at 166,000 tons [24]. In the future, a further rapid growth in PAB is expected. High temperature resistant and/or electrically conductive resins will lead the way. Low temperature impact properties should also enjoy a wider attention. Commercial EPB's are listed in Table 3. About 20% of ER are sold as blends.

In general the main goal for development of EPB is to replace metals. In this respect the impact of EPB on automobile, aerospace and business machines/appliances markets is the greatest. As an example the plastic content of a small US car from 1980 to 1990 will double. By the year 2000 nearly 1.4 million tons of plastics will be used in the automobile industry [25,26].

As indicated in Table 4 there is also a continuous displacement of one type of plastic by another with a growing tendency for higher content of EPB. A similar tendency is observed in other industries (Table 5).

EPB's can be divided into two categories: A. blends of ER with a commodity resin, and B, blends of two engineering resins. Examples of blends A are: PPE with polystyrene or with high impact polystyrene, HIPS, PC with ABS, SMA or MAM, ER/elastomer, polysulfone/ABS, etc. The type A constitute about 90% of all EPB, with the remaining 10% belonging to type B. Examples of type B are: PET with PBT, PC with PBT or PET, polysulfone with PET or PBT, PPE

Table 6. SELECTED RECENT US PATENTS ON POLYAMIDE BLENDS

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	3, 920, 602/ Nov. 18, 1975	Celanese	PA-66/ 5 to 60wt% GF/0.5 to 3wt% Phenoxyl	Tensile strenght and Izod Impact
2.	4, 242, 470/ Dec. 30, 1980	Shell	PA's/1 to 29wt% Block Polymer (SEBS, SEPS...) with viscosity ratio at $\dot{\gamma} = 100\text{s}^{-1}$ from 0.8 to 1.2	Dry impact strength
3.	4, 283, 502/ Aug. 11, 1981	Du Pont	PA-66/< 1% of adduct maleic or fumaric acid	Enhanced crystallinity leading to improved tensile strength and dimensional stability.
4.	4, 287, 315/ Sept. 1, 1981	Krefeld	PA-6 or PA 66/1 to 30wt% copolymer of ethylene, acrylamide and acrylic acid ester	Impact strength
5.	4, 292, 416/ Sept. 29, 1981	Phillips	PA's/0.01 to 10wt% polyacrylene sulfide	Moldability, impact strength and warpage resistance
6.	4, 317, 891/ Mar. 2, 1982	Sumitomo	1 to 10wt% PA/(PC + ABS, MBS or ABSM in 1:1 to 4:1 ratio)	Moldability, solvent resistance, paintability and impact strength
7.	4, 320, 213/ Mar. 16, 1982	Monsanto	PA/3 to 50wt% hydroxyl functional elastomer/0.1 to 10wt% succinic functional copolymer	High impact strength
8.	4, 346, 194/ Apr. 24, 1982	Du Pont	PA-66 blend with PA-6 in ratio 1:4 to 4:1/3 to 40wt% EPDM-fumaric acid	Low temperature toughness

Table 6. SELECTED RECENT US PATENTS ON POLYAMIDE BLENDS (CONT.)

No.	Patent No./ Date	Assignee	Composition	Advantages
9.	4, 381, 371/ Apr. 26, 1983	Bayer	Amorphous PA/5 to 30 wt% ABS	Toughness, rigidity, impact and high tracking resistance (for automobile and E/E application)
10.	3, 391, 956/ Jul. 5, 1983	Polymer Corp.	PA-6/5 to 50 wt% polyester elastomer (HYTREL)	Impact strength, increased viscosity and melt strength for enhanced processability
11.	4, 347, 332	American Can. Co.	PA-6/10 to 80wt% EVOH copolymer/ 2 to 25 wt% plasticizer (e.g. PA-11)	Low temperature film extrudability, improved adhesion between layers, high strength, toughness and oxygen barrier properties
12.	4, 404, 317/ Sept. 13, 1983	Du Pont	Semicrystalline PA (e.g. PA-66)/ 2 to 95 amorphous co-polyamide based on phthalic acids	Transparency, low flammability, solvent/acid resistance, high flexural modulus at 50%RH, etc.
13.	4, 438, 236/ Mar. 20, 1984	ICI	PA-66/0.5 to 5 wt% LCP (broad claims for most engineering and blends)	Processability (at lower temperature, at least 10% lower shear viscosity)
14.	4, 501, 861/ Febr. 26, 1985	Monsanto	PA-6/15 to 85 wt% block polymer of ϵ -coprolactam with either propylene oxide, isoprene, dialkyl silane or other flexible block	Impact strength
15.	(PCT)W084/03894	General Electric	PA-66/40 to 80 polyether imide	Tensile, flexural impact strength and HDT

Table 7. SELECTED RECENT US PATENTS ON POLYCARBONATE BLENDS

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	4, 122, 131/ Oct. 24, 1978	General Electric	PC/1 to 40 wt% PE/ 0 to 20 wt% SEBS	Flowability, stress crack resistance and impact strength
2.	4, 188, 314/ Febr. 12, 1980	General Electric	PC/25 to 75 wt% polycyclohexane- dimethanol phthalic esters	Solvent resistance, transparency, impact strength, with stable dimensions and lower processing temperature
3.	4, 218, 544/ Aug. 19, 1980	Dow	PC/10 to 62 wt% anhydride copolymer/2 to 50 wt% SAN/5 to 25 wt% butadiene	Flowability, impact strength and heat resistance
4.	4, 226, 961 Oct. 7, 1980	General Electric	PC/10 to 85 wt% of PET and/or PBT/5 to 50 wt% aromatic polyester carbonate	Processability, ductility and transparency
5.	4, 243, 764/ Jan. 6, 1981	Dow	PC/10 to 60 wt% ABS	Melt flow properties, impact strength and heat resistance
6.	4, 335, 032/ Jun. 15, 1982	General Electric	PC/2 to 7 wt% PE/0.2 to 2 wt% PDMS	Melt flow and impact strength
7.	4, 350, 799/ Sept. 21, 1982	Mobay	PC/0.5 to 80 wt% polyphosphonate/polyurethane	Flame resistance
8.	4, 358, 563/ Nov. 9, 1982	General Electric	PC - aliphatic ester terminated/ 4 to 6 wt% PE or PP	Thick section impact strength
9.	4, 358, 569/ Nov. 9, 1982	General Electric	PC or copolyester carbonate/poly-sulfone in a ratio 1:3 to 3:1	High impact strength and flame retardancy

Table 7. SELECTED RECENT US PATENTS ON POLYCARBONATE BLENDS (CONT.)

No.	Patent No./ Date	Assignee	Composition	Advantages
10.	4, 367, 310/ Jan. 4, 1983	General Electric	PC/5 to 25 wt% butadiene/10 to 62 wt% SMA/2 to 50 wt% ABS	Melt flow properties, impact strength and heat resistance
11.	4, 390, 657/ Jun. 28, 1983	General Electric	PC/5 to 45 wt% ABS/0.5 to 40 wt% MBA (Acryloid)	Impact strength, ductibility, improved aging characteristics high welding strength
12.	4, 393, 169/ Jul. 12, 1983	Dai-ice1	PC/5 to 95 wt% SMA/1 to 20 wt% styrene-diallyl maleate-butadiene-methyl methacrylate copolymer (CEVIEN)	Shock and resistance (For bus-ness machines, cars, E/E and helmets)
13.	4, 397, 982/ Aug. 9, 1983	General Electric	PC/2 to 8 wt% LLDPE/2 to 4 wt% of MBA (Acryloid)	Low temperature impact, weld line strength, low viscosity, heat stability, chemical resistance and reprocessability
14.	4, 410, 662/ Oct. 18, 1983	Mobay	PC/0.1 to 50 wt% polyanhydride or its imidized derivative (e.g. PA-18)	Impact strength
15.	4, 472, 554/ Sept. 18, 1984	Mobay	PC/5 to 95 wt% ABS and/or SAN/0.1 to 15 wt% acidic polymer or copolymer (e.g. AC540 ethylene-acrylic acid copolymer)	Flowability, tensile and impact strength, elongation and stability
16.	4, 482, 672/ Nov. 13, 1984	Bayer	PC/1 to 99 wt% PBT or PET/1 to 30 wt% SAN or ABS/4 to 15 wt% ethylene-acrylic acid copolymer	High multiaxial impact strength, high HDT (Vicat B 110°C)

Table 7. SELECTED RECENT US PATENTS ON POLYCARBONATE BLENDS (CONT.)

No.	Patent No./ Date	Assignee	Composition	Advantages
17.	W080/00027 10 Jan. 1980	General Electric	PC/5 to 80 wt% PS/0 to 25 wt% MBS	Flowability, processability, tensile strength, HDT
18.	W080/00084 24 Jan. 1980	General Electric	PC/poly(carbonate-co-organo siloxane) in an amount of about up to 50% by weight of PC	Flame retardance, ductility, solvent resistance
19.	W084/04752 6 Dec. 1984	General Electric	PC/50-95 wt% polyether imide	HDT, flexural impact and tensile strength.

Table 8. SELECTED PATENTS ON POM BLENDS

No.	Patent No/ Date	Assignee	Composition	Advantage
1.	US 4,181,685/ Jan. 1, 1980	Hoechst	POM/0.001 to 10 wt% branched or crosslinked POM	Small spherulites, hardness, stiff- ness and tensile strength
2.	US 4,351,916/ Sept. 28, 1982	DuPont	POM/0.1 to 10 wt% PEO/ 0.15 to 3 wt% PA-66	Thermal stability
3.	US 4,424,308/ Jan. 3, 1984	Celanese	POM/1 to 20 wt% PB (3% optimum)	Tensile and impact strength
4.	Europ. 0038,881/ Apr. 22, 1980	Cyanamid	POM/80 to 95 wt% PU-elastomer	Melt strength in bottle blowing
5.	Europ. 0124,879/ May 3, 1984	Mitsui	POM/4 to 50 wt % poly- (α -olefin) modified by grafting unsaturated carboxylic acid, e.g. maleated LLDPE	Toughness, impact strength, heat stability, weath- erability, molda- bility and good resistance to de- lamination

Table 9. SELECTED, RECENT PATENTS ON THERMOPLASTIC POLYESTER BLENDS

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	US 4, 290, 937/ Sept. 22, 1981	General Electric	PBT/0.25 to 4.5% PE or PE-copolymer /0.02 to 0.5% talc	Mold releasability
2.	Can. 1, 123, 534/ May 11, 1982	General Electric	PBT and/or PET/2.5 to 50% of PC and butylacrylate rubber (e.g. Acryloid)	Impact, tensile strength, modulus and HDT
3.	Eur. 0, 071, 773/ July 7, 1982	General Electric	PBT/10% PB/5% LDPE/5% PC	Impact strength
4.	US 4, 369, 280/ Jan. 18, 1983	General Electric	PBT/0.1 to 4.5% EVA/0.1 to 4.5 PE	Impact strength and low density
5.	Eur. 0, 088, 263/ Feb. 19, 1983	General Electric	PBT/1 to 20% Poly(2-methyl-1,3-propyl terephthalate)	Moldability, crystallization rate, uniformity and gloss
6.	Eur. 0, 107, 048/ Sept. 22, 1983	General Electric	PET/51 to 97% PC/3 to 20% poly (methyl n-butyl acrylate), e.g. Acryloid/0.5% LLDPE/flame retardant	Moldability, impact strength, flammability
7.	Eur. 0, 113, 096/ Dec. 19, 1983	General Electric	PET/≤ 60% impact modifier: 10 to 15% polyacrylate rubber and 10 to 15% PC	Impact strength, tensile strength and tensile strain. Recyclable
8.	Eur. 0135, 677/ June 23, 1984	General Electric	PET and/or PBT/5 to 95% ABS (Rovel)	Gloss and solvent resistance

Table 9. SELECTED, RECENT PATENTS ON THERMOPLASTIC POLYESTER BLENDS (CONT.)

No.	Patent No./ Date	Assignee	Composition	Advantages
9.	Eur. 0042, 724; Eur. 0042, 737; US 4, 346, 195; US 4, 388, 446	Ethyl Corp.	PET/10 to 90% SMA or rubber modified SMA (e.g. Dylark)	HDT
10.	US 4, 397, 986/ Aug. 9, 1983	Ethyl Corp.	PET/5 to 75% SAA	HDT
11.	Eur. 0025, 920/ Sept. 4, 1980	Rohm and Haas	PET/1 to 50% PC/4 to 25% core-shell butyl acrylate based impact modifier	Impact strength
12.	US 4, 351, 758/ Sept. 28, 1982	Celanese	PET:PBT blend in a ratio 1:1 to 9:1 with nucleating and reinforcing agents	Gloss, HDT
13.	US 4, 020, 126/ Apr. 26, 1977	DuPont	PET/1 to 5% terpolymer of ethylene, vinylacetate and methacrylic acid	Moldability, freedom from brittleness and sagging
14.	US 4, 119, 607/ Oct. 10, 1978	Shell	PBT/4 to 40% SB or SBS block polymers/48 to 55% dissimilar thermoplastic, viz. PA, PC, POM, PP, PU...	Partially co-continuous network blends with high impact strength and HDT
15.	US 4, 219, 628/ Aug. 26, 1980	Eastman Kodak	PBT/10% EPR/10% ionomer (e.g. Surlyn)	To lower the molding temperature and to increase notched Izod impact strength at low temperature

Table 9. SELECTED, RECENT PATENTS ON THERMOPLASTIC POLYESTER BLENDS (CONT.)

No.	Patent No./ Date	Assignee	Composition	Advantages
16.	Eur. 0039, 155/ Apr. 8, 1981	Asahi	PET/0.05 to 10% PA or polyhydrazine as nucleating agent	Rapid crystallization of PET
17.	US 4, 303, 573/ Dec. 1, 1981	DuPont	PET/2 to 20% ionomeric terpolymer /2 to 20% carboxylated EPDM	Reduction of brittle failure, impact strength
18.	US 4, 317, 764/ Mar. 2, 1982	DuPont	PBT/0.1 to 10% polytetramethylene oxide /3 to 35% PE with acid or ester groups	Impact strength
19.	US 4, 342, 846/ Aug. 3, 1982	Stauffer	PET or PBT/10 to 30% polybutylacrylate - SA interpolymer	Impact strength
20.	Eur. 0135, 904/ Sept. 17, 1984	Mobay	PET/5 to 61.5% PC/5 to 50% butadiene copolymer (e.g. MBS)/0.1 to 4% talc	Low warpage and high impact strength
21.	US 4, 485, 212/ Nov. 27, 1984	Uniroyal	PBT/25 to 55% EP rubber grafted with styrene and acrylonitrile	Hardness and impact strength
22.	US 4, 493, 921/ Jan. 15, 1985	Uniroyal	PBT/20 to 40% PC/20 to 30% graft copolymer of styrene and acrylonitrile on EPDM	Hardness, stiffness and impact strength
23.	US 4, 283, 326/ Aug. 11, 1981	GAF	PBT with 0 to 50% PET/15% acrylic impact modifier (KH)/mica and/or glass fiber	Dimensional stability and impact strength

Table 10. RECENT, SELECTED PATENTS ON POLYPHENYLENE ETHER BLENDS

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	Can. 1, 065, 091/ Oct. 23, 1979	General Electric	PPO/30 to 65 wt% SBS/ 5 to 25 wt% hydrogenated SBS (e.g. Kraton)	Impact strength and flame retardance.
2.	US 4, 196, 116/ Apr. 1, 1980	General Electric	PPO/20 to 80 wt% EPDM-modified PS/1 to 20 wt% hydrogenated S-B block polymer.	Impact strength
3.	Fr. 2, 483, 444/ 27 May 1981	General Electric	PPO/15 to 85 wt% poly(styrene-co-bromostyrene)	Flammability, UV-stability
4.	US 4, 277, 575/ Jul. 7, 1981	General Electric	PPO/35 wt% PS/15 wt% hydrogenated S-B and/or SEBS (e.g. Kraton)	Impact strength
5.	Eur. 0, 044, 703/ 15.07.81	Asahi-Dow	PPO/5 to 95 wt% poly(styrene-co-N-phenylmalein imide)/0 to 90 wt% hydrogenated or not S-B, SEBS	Impact strength
6.	US 4, 284, 735/ Aug. 18, 1981	Arco	PPO/50±15 wt% terpolymer of rubbery block polymer + maleimide + styrene	Impact strength
7.	US 4, 309, 514/ Jan. 5, 1982	General Electric	PPO/1 to 50 wt% teleblock polymer of styrene and saturated butadiene units (Solprene)	Impact Strength
8.	US 4, 313, 864/ Febr. 2, 1982	General Electric	PPO/10 to 30 wt% aromatic phosphate plasticizer/10wt% Solprene	Melt flow, fire retardancy, impact strength and gloss.
9.	US 4, 322, 506/ Mar. 30, 1982	Phillips	PPO/conjugated diene-mono vinylarene copolymer (Solprene)	Solution blending process leading to improved mechanical properties

Table 10. RECENT, SELECTED PATENTS ON POLYPHENYLENE ETHER BLENDS (CONT.)

No.	Patent No./ Date	Assignee	Composition	Advantages
10.	(PCT) WO 82/01885/ 10 June 1982	General Electric	PPO/17 to 83 wt% PS/3 to 15 wt% butadiene membrane	Impact strength
11.	US 4,360,618/ Nov. 23, 1982	Monsanto	PPO/10 to 90 wt% of SAN or ABS, containing 2 to 8% AN	HDT and impact strength
12.	(PCT) WO 82/04056/ 25 Nov. 1982	Western Electric	PPO-PC copolymer/5 to 95 wt% PS or HIPS	Thermal/oxidative/dimensional stability, electrical insulating and mechanical properties
13.	Eur. 0,083,049/ Dec. 18, 1982	General Electric	PPO/1 to 25 wt% PS grafted EPDM/0 to 20 wt% PS/1 to 35 wt% triarylphosphate	Improved integrity of moldings (lack of delamination), gloss, ductility and tensile strength
14.	US 4,371,672/ Febr. 1, 1983	Atlantic Richfield	PPO/phosphorus containing alternating copolymer of styrene and propylene oxide	Miscible blend
15.	Eur. 0,086,448/ Febr. 24, 1983	General Electric	PPO + HIPS/20 to 80 wt% terpolymer of styrene, butadiene and caprolactone	Impact strength
16.	Eur. 0,088,293/ Mar. 28, 1983	General Electric	PPO with or without HIPS/0.1 to 5 wt% poly(ethylene-co-methyl acrylate)	Impact and tensile strength
17.	US 4,387,189 Jan. 7, 1983	BASF	PPO reacted with reactive copolymers of S, AA and MA/PS or HIPS	Processability, impact strength and HDT

Table 10. RECENT, SELECTED PATENTS ON POLYPHENYLENE ETHER BLENDS (CONT.)

No.	Patent No./ Date	Assignee	Composition	Advantages
18.	US 4,389,511/ Jun. 21, 1983	Monsanto	PPO/10 to 90 wt% poly(styrene-co-4 ter butylstyrene) modified with rubber	Miscible blends of good ductility tensile strength, impact strength and HDT
19.	US 4,405,753 Sep. 20, 1983	Monsanto	PPO/10 to 30 wt% SAN or ABS/10 to 30 wt% SMA	Impact strength and HDT
20.	(PCT) WO 83/03422 13 Oct. 1983	General Electric	PPO/10 to 90 wt% polyetherimide	Impact strength and mechanical properties
21	Eur. 0,129,825 18.06.84	General Electric	PPO/ 30 wt% PA/1 to 20 wt% organic phosphate	Compatible, flame retardant blend
22.	Eur. 0,133,487 14.07.84	General Electric	PPO/ 20 wt% PE modified by SB, SBS or hydrogenated SB	Tensile and impact strength, ductility, absence of delamination
23.	Eur. 0,138,599 12.10.84	Mitsubishi	PPO/10 to 30 wt% PS/2 to 15 wt%, nitrile rubber/2 to 10 wt% butyl rubber/5 to 20 wt% aromatic phosphate	Impact strength, HDT and flame retardancy
24.	US 4,480,073 Oct. 30, 1984	Mobil Oil	PPO/20 to 99 wt% poly(butadiene-g-methylethyl benzene)	Compatible blends
25	US 4,491,649 Jan. 1, 1985	Borg-Warner	PPO copolymers/2 to 25 wt% ABA/5 to 50 wt% PC	Toughness, reduced notch sensitivity and HDT

with PA, etc.

RECENT PATENTS ON EPB

The patent literature on PAB is rich in number and information. Worldwide, each year there are about 4,500 new patents, out of which about 1,000 deal with EPB. The patent literature in Japan is particularly voluminous. Of course, the patent seldom gives a hint of the economic reason or discusses the process involved in achieving claimed results.

Patents on EPB mainly protect the compositions. Even for applications where the size and orientation of dispersed phase are crucial the processing criteria are omitted. In most cases improvements are claimed in processability and mechanical properties, especially as far as impact strength is concerned.

As an example, in Tables 6 to 10 selected recent patents on EPB blends are listed. Their economic importance can be illustrated with PPO blends. During 1984 the world sales of these materials (about 200 ktons or \$700 million) has been for: business machines (30%), appliances (16%), electrical/electronics (13%) and transport industry (11%).

As evidenced from quoted patents, the most important aspects of the technology are the impact strength, processability, stability and mechanical properties. For each of the five "workhorse" ER, there are recent

Table 11. BLENDING FOR PROPERTY ENHANCEMENT; EXAMPLES SELECTED FROM
RECENT PATENT LITERATURE

No	Property	Matrix Resin	Modifying Resin
1.	Impact	PVC, PP PE, PC PA, PET PPE	ABS, SBS, SEBS, EPR, EPDM, PBR, SAN, ASA, SMA, MBA, PE, HIPS
2.	HDT, stiffness	PC, PA, SAN, ABS	PET or PBT, PEI, PPE, PC, PSF
3.	Flame retardancy	ABS, Acrylics PA PC PPO	PVC, CPE, semi-aromatic-PA polyphosphates, PSF copolysiloxanes copolybromostyrene
4.	Chemical and solvent resistance	PA, PC PPO	ABSM, copolysiloxanes polyphosphates PVC, PA, PET
5.	Barrier properties	Polyolefins	PA, EVOH
6.	Processability	PPE Thermoplastics PET, PC PVC PA	PS and its copolymers LCP, PU PA, PE, PBR, MBS CPE, Acrylics PSF, EVOH

Table 12. SELECTED PROPERTIES OF UNFILLED ENGINEERING RESINS AND BLENDS

No	Resin or Blend	Commercial Name	Elong. %	Flex. Mod. (GPa)	Tens. Str. (MPa)	Notched Impact Str (J/m) 23°C	HDT (1.82MPa, °C)
1.0	PC	Lexan	90	2.20	56	640	132
1.1	PC/ABS	Bayblend	50	2.20	45	640	105
1.2	PC/ABS	Pulse	100	2.59	53	530	96
1.3	PC/SMA	Arloy	80	2.20	45	640	121
1.4	PC/PET	Macroblend	165	2.07	52	970	88
1.5	PC/PBT	Xenoy	130	2.07	56	854	121
1.6	PC/SEBS	Pat.4,122,131	-	-	61	910	139
2.0	PA-6,6	Zytel	60	2.83	83	53	90
2.1	PA/PO	Zytel-ST	60	1.72	52	907	71
2.2	PA/PPS	Pat.4,292,416	90	2.18	65	186	88
2.3	PA/CPA	Pat.4,383,084	77	3.07	77	171	119
2.4	PA/Ionomer	Pat.4,404,325	252	1.80	45	955	-
2.5	PA-6,6/PPO/ HIPS	Noryl-GTX "	60 8	2.14 7.66	60 159	215 105	143 235
2.6	PA-6,6/Elast.	Bexloy	120	2.07	62	1030	115
2.7	PA-6/ABS	Elemid	-	2.07	48	998	200
3.0	PSF	Udel	9	2.69	70	69	174
3.1	PSF/PC	Pat.4,489,181	14	2.46	62	390	180
3.2	PSF/PBT	Mindel	2.9	2.41	115	88	166
4.0	POM	Delrin	40	2.83	48	75	136
4.1	POM Copolymer	Celcon	75	2.59	43	75	110
4.2	POM/Elastomer	Duraloy	220	1.04	37	220	60
4.3	POM/Elastomer	Delrin	75	2.62	69	123	136

inventions of composition with a small quantity of polyolefin, with rubber-containing copolymers and with polymeric liquid crystals, PLC. There are also specific blends for each resin. Due to miscibility of PPE with polystyrene, PS, there is a host of blends of PPE with styrenic derivatives: copolymers, halogenated-PS, methylated-PS, etc. In PA's, compatibilization is achieved via blending with functionalized polymers: hydroxylated, maleated or poly-co-acids. In these cases a chemical reaction during processing would be the crucial step in achieving desired properties.

PROPERTIES OF EPB

Reading the patents it is surprising how few inventions seem to be truly "surprising" or "unexpected" - the terms beloved by the patent attorneys. Certain rules of blending for improvement in specific properties can be made. These are summarized in Table 11. With few exceptions, the effect of modifying resin is nonspecific; it generates similar results in several matrix polymers. There is always a complicating problem of selecting proper molecular parameters to optimize the thermodynamic and rheological effects on morphology. These aspects will be discussed later in this review.

In Table 12 selected properties of ER or their blends as quoted in commercial or patent literature are listed. Since there are many grades of each commercial blend the listed values were selected so as to represent upper grades. The data shows that significant improvements over the behavior of neat resin can be achieved by blending. Most frequently, improvement of one

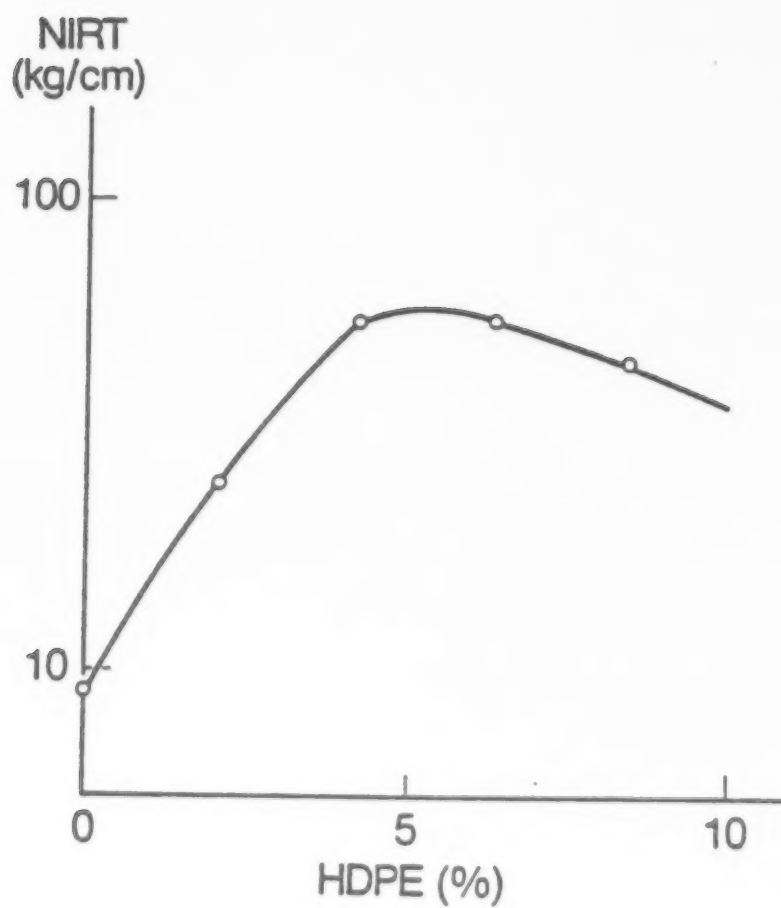


Fig. 1 Notched Izod impact strength at room temperature for polycarbonate (melt flow rate = 10.5 g/10 min) containing 0.75% of polydimethyl siloxane and indicated quantity of high density polyethylene. Blends were aged 4 hrs at 125 °C. Data: US Pat. No. 4, 335, 032 (1982) by N.R. Rosenquist, assigned to General Electric Co.

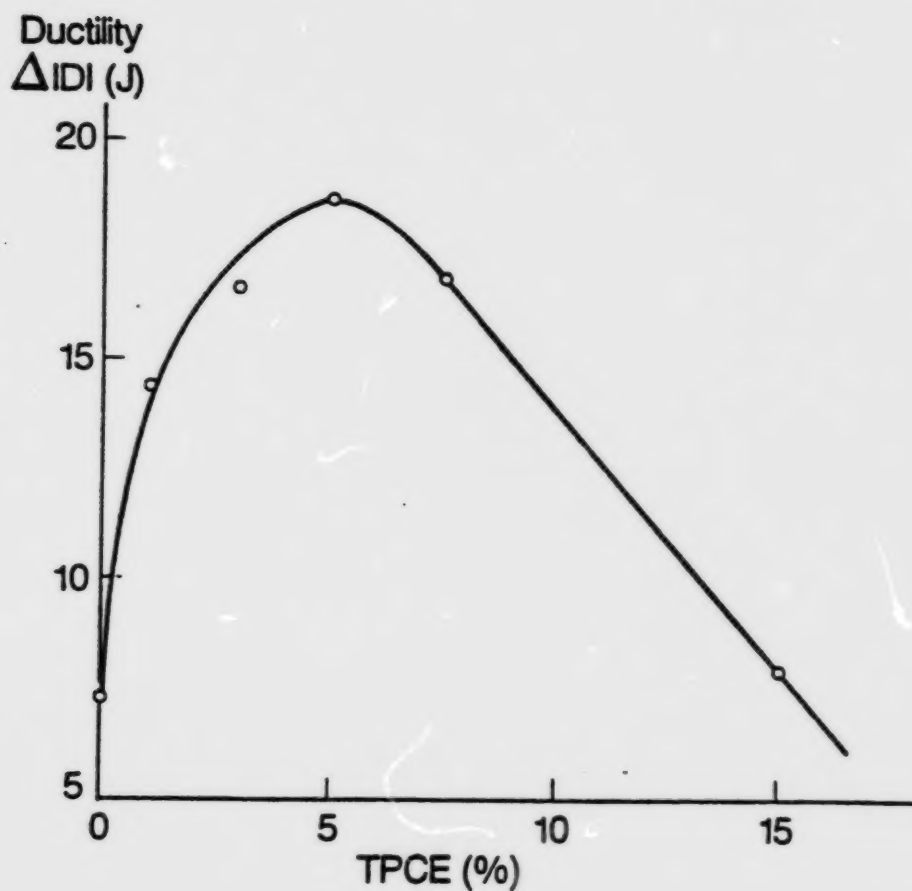


Fig. 2 Ductility (measured in a multiaxial inverted dart impact test at 23°C) versus composition for acrylonitrile-butadiene-styrene copolymers, ABS blend with thermoplastic copolyetherester, TPCE, (Nytrel 4056). Data: US Pat. No. 4, 508, 870 (1985) by D.L. Dufour and W.J. Jones assigned to Monsanto Co.

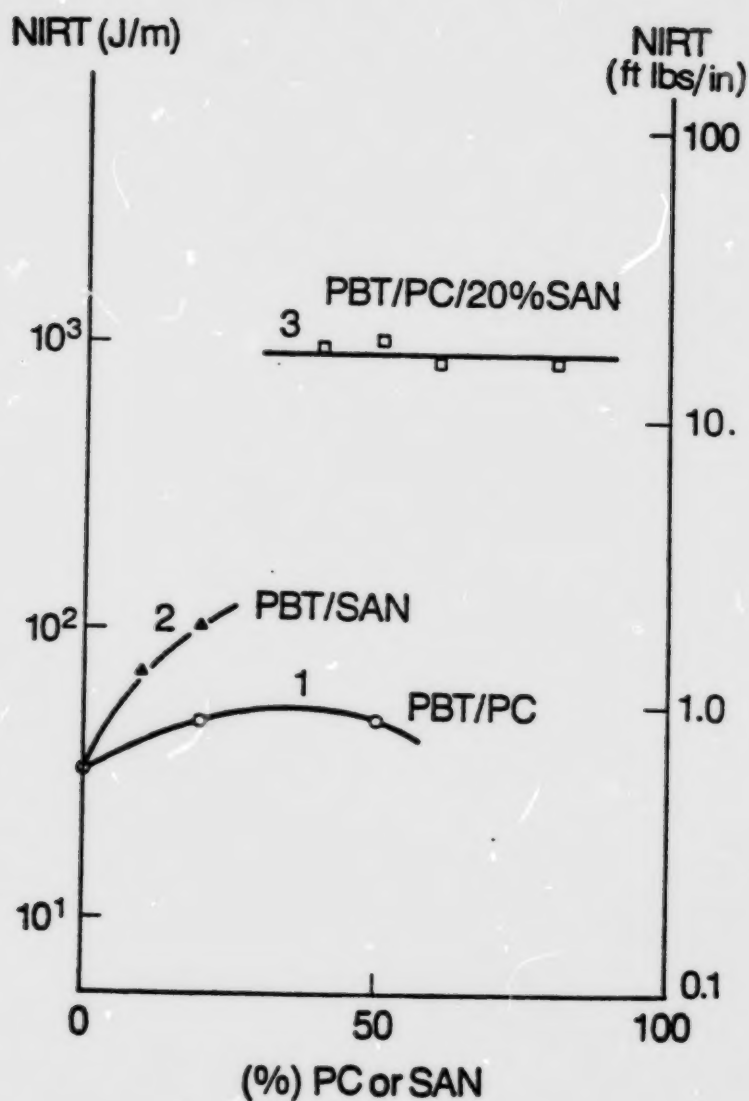


Fig. 3 Notched Izod impact strength at room temperature vs composition for blends (from bottom up):

- (1) polybutyleneterephthalate, PBT, with polycarbonate, PC;
- (2) PBT with styrene/acrylonitrile (SAN 72/28) copolymer;
- (3) PBT with PC and 20 wt% SAN.

Data: US Pat. No. 4,493,921 (1985) by J.M. Wefer assigned to Uniroyal Inc.

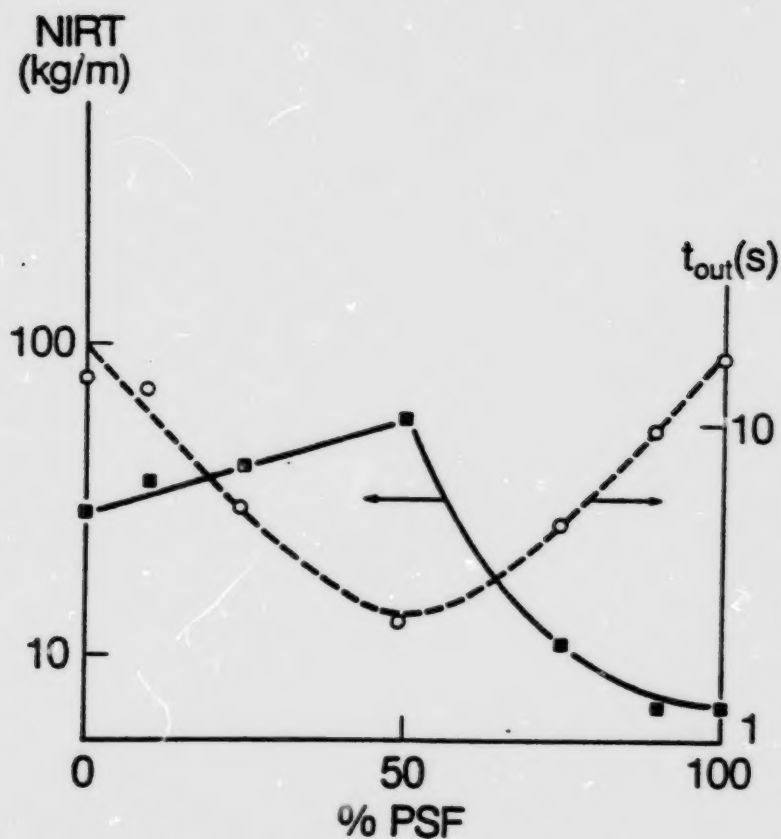


Fig. 4 Notched Izod impact strength at room temperature, NIRT, and flame-out time, t_{out} , vs composition for polyester carbonate, PEC, blend with polysulfone, PSF (Udel). Data: US Pat. No. 4, 358, 569 (1982) by C.B. Quinn and N.R. Rosenquist assigned to General Electric Co.

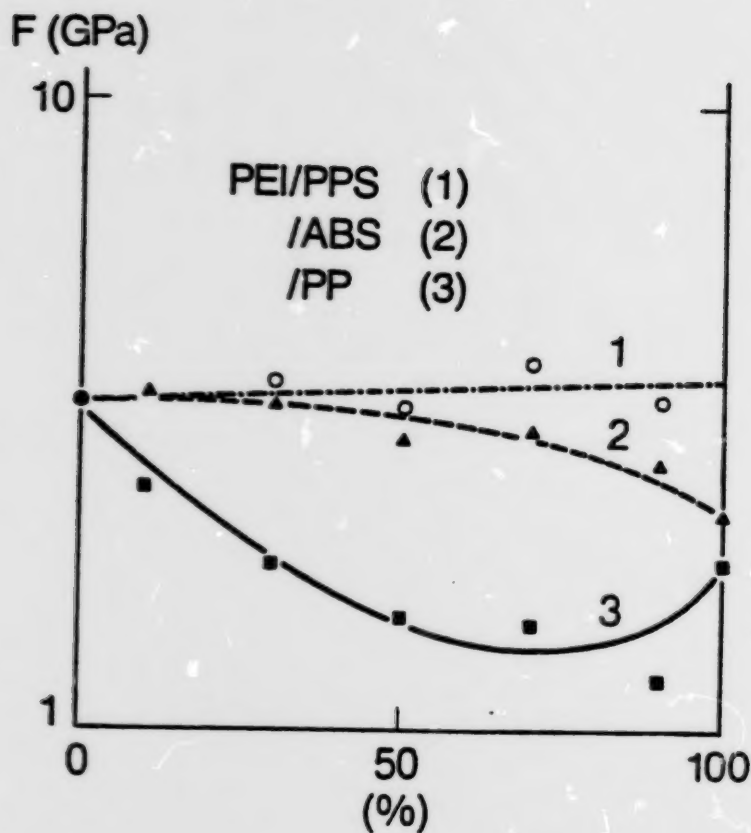


Fig. 5 Flexural modulus vs composition for polyetherimide blends with (1) polyphenylene sulfide, PPS; (2) acrylonitrile-butadiene-styrene copolymer, ABS; and (3) polypropylene, PP. Data: US Pats. assigned to General Electric Co.: (1) No. 4,445,410 (1984) by H.F. Giles, Jr. (2) No. 4,427,830 (1984) by H.F. Giles Jr. and W.R. Schlicht.

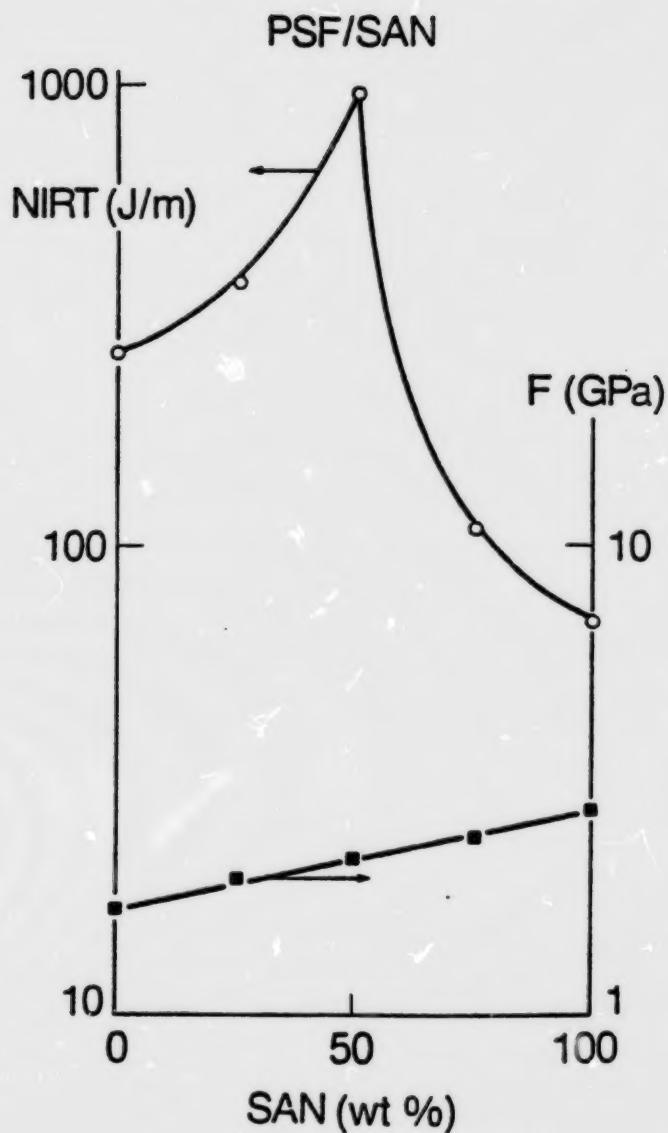


Fig. 6 Notched Izod impact strenght at room temperature, NIRT, and flexural modulus, F , vs composition for polysulfone, PSF (Udel), blended with styrene acrylonitrile interpolymer, SAN, (containing 32% acrylate, 10% crosslinked and 58% uncrosslinked SAN). Test specimens were injection molded at 274 °C. Data: US Pat. No. 4,360,636 by J. Silberberg assigned to Stauffer Chem. Co.

property leads to reduction of another. The current trend is to simultaneously optimize blend formulations in respect to several properties important for a specific application, sacrificing those which are not vital.

Certainly there are blends which do much more than anticipated on the basis of the present state of understanding, e.g. the original finding of PPO/PS miscibility, or the repeated discovery of unusually large effects upon addition to ER of small quantities (usually well below 5%) of polyolefin or elastomer on impact (Figs. 1 and 2). The truly unexpected synergistic behaviors illustrated in Figs 3 and 4 may serve as more recent ones. In the first case the three component blends of polybutyleneterephthalate, PBT, with PC and 20% of poly(styrene-co-acrylonitrile), SAN show a ten-fold improvement in the notched Izod strength at room temperature (NIRT) over the two component PBT/SAN or PC/SAN blends. In the second case a significant synergism was discovered in NIRT for the polyestercarbonate/polysulfone system.

There is intensive activity in the field of high performance blends with newer ER. The work seems to be directed mainly toward improvement of processability and obtaining broad patent protection; there are dozens of patents issued to General Electric covering the full range of concentrations of polyetherimide, PEI, with polyarylates, PC, EPDM, ABS, MBS, acrylate copolymers, polysulfide PPS, etc. The tensile (Young) modulus vs composition for PEI blends with PPS, ABS and PP are presented in Fig. 5. An impressive improvement of NIRT in PPS/SAN is illustrated in Fig. 6.

GENERATION OF STRUCTURE IN POLYMER ALLOYS AND BLENDS, PAB

The miscible polymers can be processed as single-phase polymers. Due to specific interactions the density of blends is usually higher than what can be expected from additivity. The loss of free volume is then reflected in the positive deviation from the log-additivity rule, PDB, for shear viscosity, η , the first normal stress difference, N_1 , or their equivalents in other modes of deformation, e.g. dynamic or extensional [14,27].

In immiscible PAB properties are strongly related to the interface as well as to the size and the shape of dispersed phase. The morphology is controlled by equilibrium and non-equilibrium thermodynamics as well as by the flow fields. At equilibrium, for low volume fraction of dispersed phase, $\phi \leq 0.12$, droplets are expected; above this value fibers and lamellas are usually found [28,29]. If the polymers are miscible under one set of pressure, P , and temperature, T , conditions but immiscible under another two different non-equilibrium morphologies are possible depending on the method of P, T variation. For rapid, deep quenching the spinodal decomposition, SD, mechanism will generate an interconnected, interpenetrated network system. For shallow quenching into metastable zone the nucleation and growth, NG, mechanism will result in droplet formation. Both of these structures will coarsen with time by the Ostwald ripening process leading to an appropriate equilibrium morphology [30-32].

The flow conditions superimpose another set of morphologies. Flow encapsulation of one phase by another, deformation leading to fiber or

platelet formation due to shear or extensional field, shear induced coalescence, interlayer slip and shear-controlled SD or NG are well-documented [18,33-36].

There are several guiding rules for obtaining a desired structure. These can be divided into two groups: (i) rheological and (ii) rheological coupled with interfacial tension.

(i) Rheological criteria [37-40]. In order to achieve maximum dispersion at minimum expended energy in a steady-state shear flow, η and N_1 of the two immiscible polymers should be the same. (For another type of deformation the analogous rheological functions should be used). This statement is valid only if η and N_1 are compared in the full range of shear stress generated during dispersing and processing stages. Two other parameters complicate the phenomenon. It was shown [41] that co-continuous structures are generated when

$$\phi_1/\phi_2 = \eta_1/\eta_2 \equiv \lambda \quad (1)$$

where the subscripts 1 and 2 indicate respectively the dispersed phase and the matrix. On the other hand at $\phi = \text{const}$ droplets were formed [42] in capillary as well as in rotational shear field (cone-and-plate) at shear stress:

$$\sigma_{12,c} \leq a\lambda^b \quad (2)$$

where a and b are constants dependent on ϕ and type of blend and the subscript

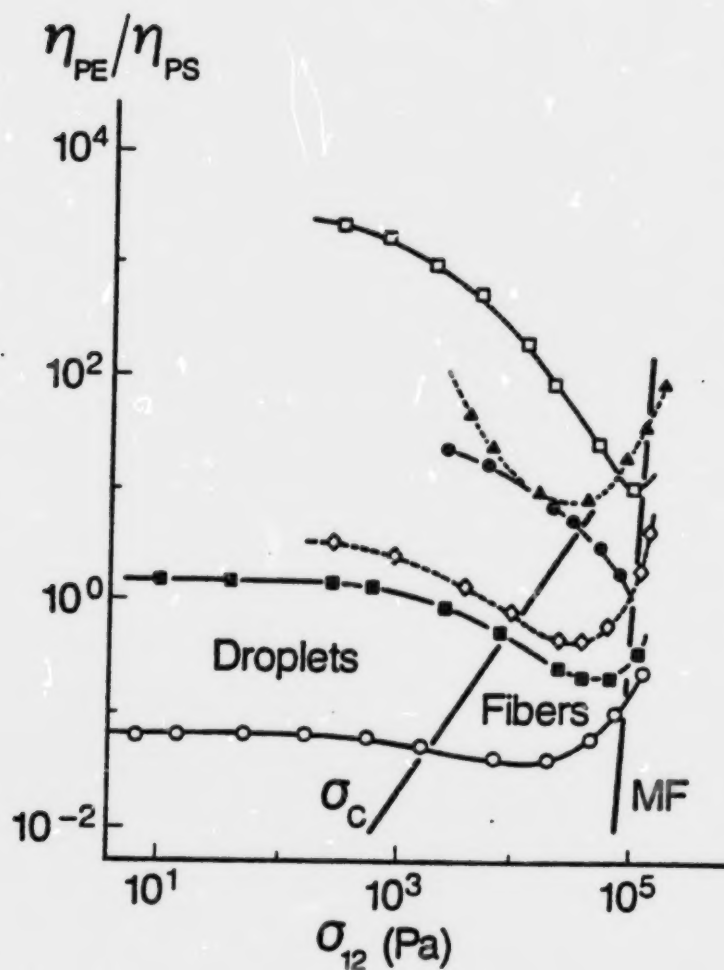


Fig. 7 Shear viscosity ratio of polyethylene, PE (minor phase, 30%) to polystyrene, PS vs shear stress, σ_{12} , at 180 °C for six PE/PS blends. Lines indicated σ_c and MF represent the limiting values for droplet formation and melt fracture, respectively. Data valid for capillary and rotational shear field [42].

c indicates a critical value. At $\sigma_{12} = \sigma_{12,c}$, up to the melt fracture region, formation of fibers was reported for PS/PE containing 1, 10 or 30 wt% of PE.

In several publications [33,39,43] it has been reported that (for both Newtonian and pseudoplastic liquids) droplets can be formed only if $\lambda < 4$; above this limit fibers were obtained. These observations do not agree with data in Fig. 7, where droplets are reported for $0.04 \leq \lambda \leq 2000$. The disagreement illustrates the complexity of the situation - shear stress level, relative rheological properties of the two liquids, composition and most of all uniformity of deformational field must be considered.

(ii) Rheological-interfacial criteria. To the second group of criteria belong the dependencies in which the interfacial tension, v , is taken into account. Here, first the Van Oene's relation should be discussed [44]:

$$v = v_0 + (d/12)(N_{1,1} - N_{1,2}) \quad (3)$$

In the relation d stands for diameter of a droplet (polymer 1) and $N_{1,i}$ for N_1 of liquid $i = 1$ or 2 . At equilibrium $v = v_0$. Van Oene's relation has three interesting features:

1. For $N_{1,1} > N_{1,2}$ the interfacial tension increases with shear stress, i.e. droplets are becoming more difficult to break. For $N_{1,1} < N_{1,2}$ there is a reduction of the interfacial tension and enhancement for generation of fine dispersion at high shear stress.

2. Since $v > 0$ Eq (3) predicts conversion from droplet to a continuous morphology (reduction of the interfacial area) at:

$$N_1 2 = N_1 1 + 12v_0/d \quad (4)$$

3. The above two features lead to complementarity of polymer blend pairs: if at low content of polymer A in B a droplet dispersion is observed, at low content of B in A a continuous (fibers or lamellas) morphology is to be expected.

Eq (3) neglects numerous aspects influencing PAB morphology. It is, however, an invaluable tool directing development of structured PAB when the other factors are kept constant. While Van Oene considered the influence of a difference in N_1 on non-equilibrium interfacial properties Choi and Showalter [45] and later Acrivos and Lo [46] concentrated on correlation between shear stress, σ_{12} , droplet diameter, interfacial tension, and the viscosity ratio:

$$\sigma_{12} d \lambda^{1/6} / v \leq 0.148 \quad (5)$$

If in a given range of shear stress $\lambda = \text{const}$ and $v = v_0$ is assumed, then d should be inversely proportional to σ_{12} . For a series of different PAB's processed under similar condition, d should be proportional to v . The latter correlation was experimentally verified by Wu [47].

The use of Eqs (4) and (5) is difficult due to lack of simple and rapid methods for v -determination. In commercial polymers due to presence of

additives (lubricants, processing aids, stabilizers, antioxidants, etc.) the use of a general value is meaningless. There is a desperate need for a reliable experimental method of measurement of the interfacial tension using the actual resins to be blended.

In general, the "predictive" relations are valid only for steady state flow of specified nature (e.g. shearing, extension). The parameters (e.g. η , $\dot{\gamma}$, N_1 , v) used in these relations must be valid under full range of considered flow conditions. The conditions must be uniform within the sample, i.e. they may not hold for die or capillary flow. The morphology must not be affected by other factors i.e. phase ripening or crystallization. Eqs (2) to (5) are valid at low concentration $\phi \leq 0.3$. Above this limit co-continuous structures predominate.

Finally, it is worth stressing the dynamic character of the flow induced morphologies. It is not only important to generate the desired structure but also to preserve it. The rate of reverting to equilibrium depends on the magnitude of the driving forces (mainly v_0) and the barrier heights (e.g. the diffusion constant D). To stabilize the structure both factors: reduction of v and increase of D must be considered. It has been demonstrated [18] that in semi-crystalline polymer blends there is a possibility of generating fibrillar morphology at T well below the melting point of dispersed polymer. Due to the presence of crystallinity, once formed the structure remains stable.

Table 13. COMPATIBILIZATION OF POLYMER BLENDS

1. Prevent segregation by:

- (i) promoting co-crystallization
- (ii) cross-linking the dispersed phase (dynamic vulcanization)
- (iii) forming interpenetrating networks producing a mechanical interlock of the phases
- (iv) ionic interactions (ion-ion or ion-dipole)
- (v) hydrogen bonding

2. Use of compatibilizers

- (i) block copolymers
- (ii) graft copolymers
- (iii) co-solvents

3. Reactive polymer processing

- (i) polymerization
- (ii) functionalization
- (iii) polymer-polymer reactions
- (iv) (semi) interpenetrating networks

PROCESSING PAB

Processing can be divided into: blend/alloy preparation (compounding) and forming. Most of compounding is done by resin manufacturers (65%), some by companies specializing in compounding (25%) and the rest by processors. Compounding, even on a large scale, adds between 15 and 30 cents/kg to the cost of material [9,13].

PAB are prepared by mechanical mixing, dissolution in co-solvents, latex mixing, dissolution of one polymer in the monomer of the second blend component, and by diverse methods used in interpenetrating network, IPN, technology [48]. Since mechanical blending predominates, only this aspect will be considered.

Preparation of stable PAB can be compared to that of a stable emulsion, the difference being the non-Newtonian, viscoelastic character of polymer melt and higher temperatures. The two liquids as well as a selected "emulsifier" should be added in proper sequence and proportions, homogenized and quenched. For homogenization high shear and extensional rates of deformation should be used, e.g. $\dot{\gamma} > 10^3$ and $\dot{\epsilon} > 5(s^{-1})$, respectively. The fields should have uniform and precisely controlled T, P and residence times, τ . To avoid degradation τ should be small.

In PAB the role of emulsifier is played by compatibilization, methods of which are listed in Table 13. Depending on the final application an addition of a compatibilizer or irreversible crosslinking may be selected.

Table 14. COMPOUNDING EQUIPMENT USED IN PREPARATION OF PAB

- A. Batch Mixers: (i) roll mills
(ii) internal mixers
(iii) kinetic mixers
- B. Continuous : (i) single screw extruders
Mixers (ii) twin-screw extruders
(iii) single-shaft intensive mixers
(iv) twin-shaft continuous intensive mixers
(v) disk extruders
(vi) motionless mixers
(vii) others

Compatibilization via reactive processing merits special comment. The method may generate a controlled amount of compatibilizing co-polymer or it can result in a network formation. To the first category belong: the recently developed catalytic system which allows a block copolymer formation during extrusion of polyamide-6,6 and PET [49], a commercial functionalization of e.g. PS (Dow), elastomers (DuPont) or PP (Hercules), a transesterification of e.g. PBT with PC (GEC) or polyarylates with PET (UC), etc. The reactive processing, due to solventless reaction at high T and P, is rapid and efficient. On the one hand it allows significant saving on capital costs, but on the other it requires generation of a large interfacial area, precise multi-port dosing and good control of processing parameters (P, T, τ).

The PAB compounding equipment can be divided into batch and continuous (see Table 14). If patent literature is to be a guide, the most frequently used machines are: (i) single screw extruders (usually with a preblending step), (ii) twin-screw extruders (gaining popularity) (iii) intensive mixers and (iv) others. The advantages of (i) are the cost, flexibility for changes and wide variety of types and sizes available on the market; the disadvantages are notoriously poor control of stress field and residence time as well as low rates of deformation. The twin-screw extruders (ii) are designed to overcome these disadvantages. Superior control of temperature and flow profiles, short and uniform residence time and flexibility can be obtained, but at relatively high capital cost. Both (i) and (ii) are continuous mixers easily incorporated into a multi-stage process line for large volume processing. The third type of mixer used in PAB compounding is a batch process sigma-blade or internal mixer. Its advantages are: controlled uniform shear and extensional

Table 15. SELECTED RECENT PATENTS ON SPECIALTY POLYMER BLENDS

15.1 With liquid crystal polymers (LCP)

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	US 4, 207, 407/ Jun. 10, 1980	USAF	10 to 30% rod-like aromatic polymer/coll-like heterocyclic polymer	Self-reinforcing (on molecular level) blend
2.	Eur. 0051, 933/ May 19, 1981	ICI	LCP/0.5 to 99.5% PTFE	Processability, lubricity
3.	US 4, 408, 022/ Oct. 4, 1983	Celanese	LCP/50 to 75% PET or PBT	High anisotropy/self reinforcement, economy
4.	US 4, 438, 236/ Mar. 20, 1984	ICI	LCP(0.5 to 5%)/thermoplastic resin (e.g. PES, PPO, PC, PVC, PA)	Processability
5.	US 4, 489, 190/ Dec. 18, 1984	Celanese	LCP/5 to 50% PET or PBT	Synergistic mechanical properties, economy

Table 15. SELECTED RECENT PATENTS ON SPECIALTY POLYMER BLENDS

15.2 With polyetherimide (PEI)

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	Eur. 0117, 326/ Feb. 25, 1983	General Electric	PEI/polyarylate	Processability, impact strength, flexural strength and modulus
2.	Eur. 0117, 327/ Feb. 25, 1983	General Electric	PEI/polyarylate/polycarbonate	HDT, flame resistance
3.	(PCT)W084/04752/ Dec. 6, 1984	General Electric	PEI/PC	HDT, flexural strength, tensile strength, impact strength and flame resistance
4.	US 4, 387, 193/ Jun. 7, 1983	General Electric	PEI/poly(carbonate-b-siloxane)	Impact strength, flexural properties
5.	US 4, 390, 665/ Jun. 28, 1983	General Electric	PEI/EPDM	Impact strength
6.	US 4, 393, 168/ Jul. 12, 1983	General Electric	PEI/ABS or MBS	HDT, impact strength, flexural and tensile properties
7.	US 4, 395, 518/ Jul. 26, 1983	General Electric	PEI/acrylate copolymers (e.g. Acryloid)	Processability, impact strength with high flexural, tensile strength and HDT
8.	(PCT)W083/03416/ Oct. 13, 1983	General Electric	PEI/PEI of different type	High performance, high T _g application in aerospace and transport

Table 15. SELECTED RECENT PATENTS ON SPECIALTY POLYMER BLENDS

15.2 With polyetherimide (PEI)(cont.)

No.	Patent No./ Date	Assignee	Composition	Advantages
9.	US 4, 427, 830/ Jan 24, 1984	General Electric	PEI/1 to 20% PP or PP-copolymer	Notched izod strength (maximum at 10% PP)
10.	US 4, 455, 410/ Jun. 19, 1984	General Electric	PEI/polysulfide (e.g. Ryton)	Flexural strength
11.	US 4, 468, 506/ Aug. 28, 1984	General Electric	Blend of two or more PEI's	Glass transition temperature 125 to 210°C suitable for automobile and aerospace application
12.	(PCT)W084/03894/ Oct. 11, 1984	General Electric	PEI/(40 to 80%)/PA's	Tensile, flexural strength

15.3 With Polyestercarbonate (PEC)

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	Fr. 2, 535, 332/ Nov. 3, 1982	General Electric	PEC/0.1 to 20% LLDPE	Enhanced stability against hydrolysis
2.	US 4, 464, 512/ Aug. 7, 1984			

Table 15. SELECTED RECENT PATENTS ON SPECIALTY POLYMER BLENDS

15.4 With polysulfone (PSF)

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	Fr. 2, 535, 332/ Nov. 3, 1982	Electrici- t� Fr.	PSF/20 to 40% PTPE	Processability, chemical and thermal stability (application in electrochemical cells)
2.	US 4, 360, 636/ Nov. 23, 1982	Stauffer Chem.	PSF/5 to 50% mixture of cross-linked and not SAN	Processability, tensile, flexural, impact properties and HDT
3.	(PCT)W084/04104/ Oct. 25, 1984	Union Carbide	PSF/5 to 95% SAN	Compatible blend with high moldability and high T _g
4.	US 4, 489, 181/ Dec. 18, 1984	Fox et al.	PSF/1 to 99% PC/filler	High modulus without loss of electrical properties and molten solder resistance

15.5 With polyphenylene sulfide (PPS)

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	Eur. 0062, 830/ Oct. 30, 1982	Union Carbide	PPS/10 to 90% polyaryleketone/PSO	Processability, synergistically high flexural and tensile strength
2.	US 4, 395, 512/ Jul. 12, 1983	Shin-Etsu Chem.	PPS/1 to 50% fluoro-rubber (e.g. Viton)/filler	Moldability, mechanical properties, crack and heat resistance

Table 15. SELECTED RECENT PATENTS ON SPECIALTY POLYMER BLENDS

15.5 With Polyphenylene sulfide (PPS)

No.	Patent No./ Date	Assignee	Composition	Advantages
3.	US 4, 476, 284/ Oct. 9, 1984	Phillips	PPS/1 to 30% hydrogenated SB block polymer (e.g. Solprene)	Mechanical properties, economy
4.	US 4, 497, 928/ Febr. 5, 1985	Atlantic Richfield	PPS/1 to 99% copolymer of styrene and maleimide	Moldability, tensile strength and elongation

15.6 Others

No.	Patent No./ Date	Assignee	Composition	Advantages
1.	US 4, 324, 869/ Apr. 13, 1982	Union Carbide	Polyarylate e.g. PET/1 to 5% ethylene-alkyl acrylate copolymer (e.g. EEA, EVA)/5 to 45% thermo- plastic polymer (e.g. TPE, PC, PS, PMMA, etc.)	Good hydrolytic stability, not- ched Izod, tensile strength and elongation
2.	US 4, 346, 024/ Aug. 24, 1982	Rhone- Poulenc	Polyesteramide/PA	Mechanical properties esp. impact strength

deformation fields. The disadvantages: cost, low throughput, long mixing cycle and poor batch-to-batch reproducibility.

There are other types of equipment suitable for PAB blending, e.g. compounders such as Patfoord Plastificator CRIF (also called F.N. Herstal extruder) [50] or Revertzer developed specifically for intensive mixing with short residence time. There are also general purpose extruders capable of generating excellent blends. Of these the normal stress extruder developed by Maxwell [51], FCM continuous mixer [52] and Diskpack processor [53] were reviewed recently by Tadmor et al. [54]. Furthermore, there are two new high efficiency mixing heads for single screw extruders suitable for PAB preparation; RAPRA Cavity Transfer Mixer [55] and the recently announced Dynamic Melt Mixers [56].

CONCLUSIONS

The polymer industry is changing rapidly. The development of high performance engineering resin, specialty polymers, the growing number of polymer alloys, blends and composites, as well as the increasing importance of control of polymer morphology for homopolymers and multi-phase systems will dominate the field in the years to come. Blending is vital for economic use of engineering and speciality resins (see Table 15). All these indicate the increasing importance of technical know-how not only for development's sake but for use as well. The motto of the future is "learn or perish".

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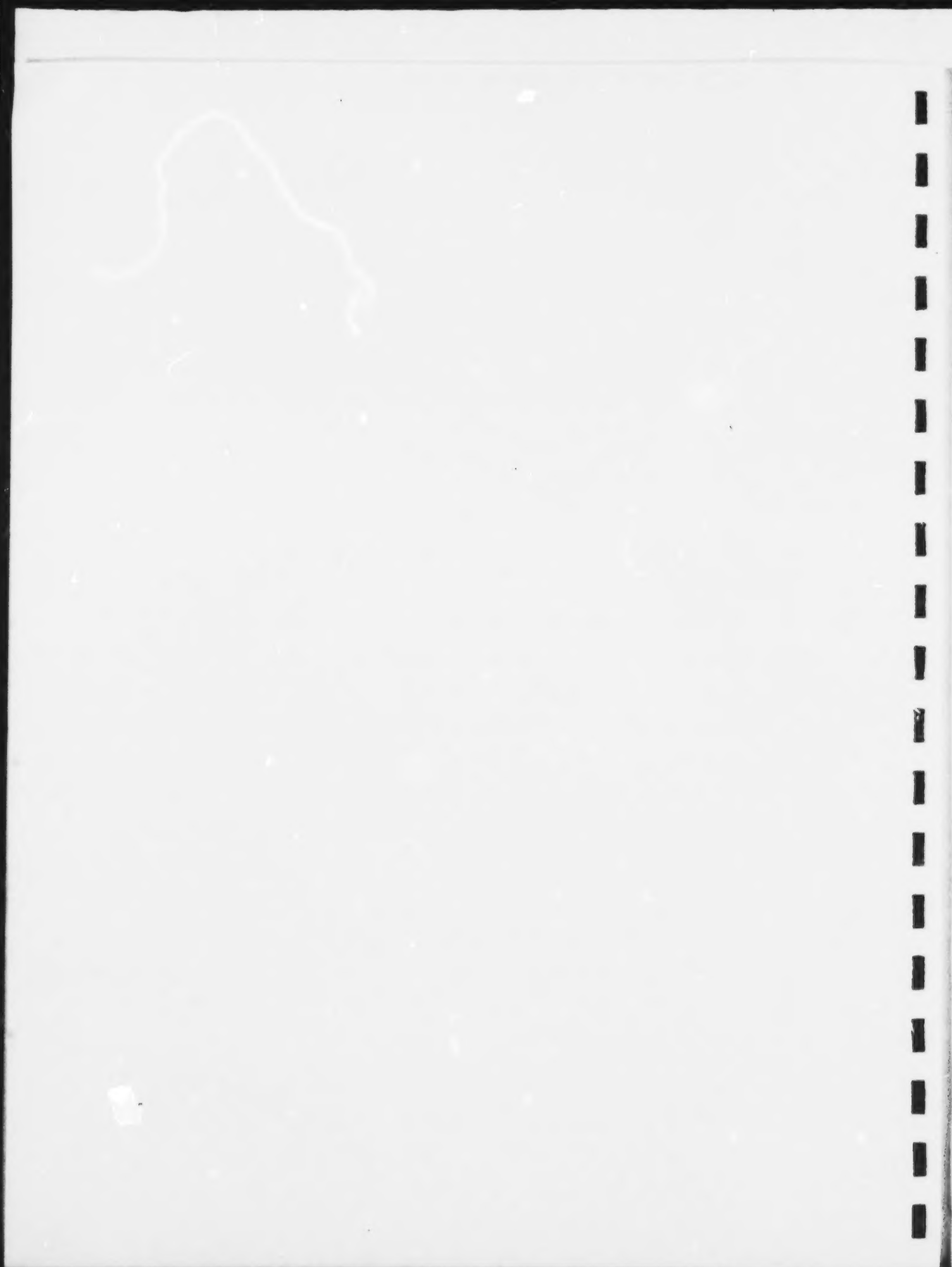
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STRUCTURE-PROPERTY RELATIONSHIPS IN
POLYAMIDE-ABS BLENDS

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ABSTRACT

The structures and physical properties of four blends of poly(acrylonitrile-co-styrene-g-butadiene) (ABS) materials with polycaprolactam (PA6) have been characterized.

The blends were separated into components by selective solvent extraction and were found to contain different structures. Blend A contained no PA6 grafts. Blend B contained PA6 grafted onto both soluble and insoluble ABS. Blend C contained PA6 grafted onto soluble poly(styrene-co-acrylonitrile) (p-SAN). In Blend D, PA6 was grafted onto both the insoluble ABS and the p-SAN phases.

Transmission electron microscopy showed different morphologies in the blends. Blend A had a co-continuous, somewhat laminar structure while Blend D consisted of an ABS phase dispersed in a PA6 continuum. Blends B and C had intermediate structures. All four blends, however, had very similar rheological and physical properties despite the variation in structure.

The study of polymer alloys and blends is an area of subject of considerable current interest. In the past, most research in the open literature centered on the preparation of miscible polymer blends, i.e., blends in which two or more polymers are combined on a molecular scale to form a single phase. These were of particular interest since thermodynamic considerations predict such systems should exist. Today, several hundred pairs of polymers have been found which are miscible either in all proportions or over limited composition ranges(1).

A second type of polymer blends which is attracting more interest today is a blend in which several phases are present but in which the interfacial energy is sufficiently low that the blend will display desirable physical properties. The term "compatible" is sometimes used for such systems. A number of such blends have been extremely important commercially since these systems frequently display an attractive combination of physical properties. In some cases, the interfacial energy between two unmodified polymers will be sufficiently low that a blend with desirable properties can be prepared by simply melt mixing the two polymers together. Examples of such systems include blends of the polycarbonate of bisphenol A with poly(butylene terephthalate) (2) or poly(acrylonitrile-co-butadiene) with poly(acrylonitrile-co-styrene) (3). In other cases, the systems must be "compatibilized" in some manner, e.g., through the preparation of an appropriate graft. The rubber modified styrenics are early examples of such systems. In such systems the interfacial energy between the rubbery polybutadiene phase and the rigid styrenic phase is reduced by chemically bonding styrenic polymer to the polybutadiene.

In some systems, essentially every polymer chain contains segments of each structure. The styrene-butadiene block copolymers are such systems. In other cases only a few of the chains contain both structures. This is the case in a typical impact modified styrenic.

A viscous mixture of two incompatible polymers subjected to a shear flow will generally form an alloy with distinct modes of dispersion. The mode of dispersion is generally dependent on differences in the rheological properties, interfacial tension, and particle size of the two phases. The most commonly observed modes of dispersion are droplets, ribbons or fibers(4). It is also known that certain conformations of these dispersions can have a synergistic effect on the properties of the alloy(5).

We wish to report characterization studies that we have carried out on four blends of polycaprolactam (PA6) with poly(acrylonitrile-co-styrene-g-butadiene) (ABS). These four blends have been separated into their various components through selective solvent extraction and each component characterized by infrared spectroscopy. In addition, the morphology, rheology, and bulk physical properties of the blends have been studied.

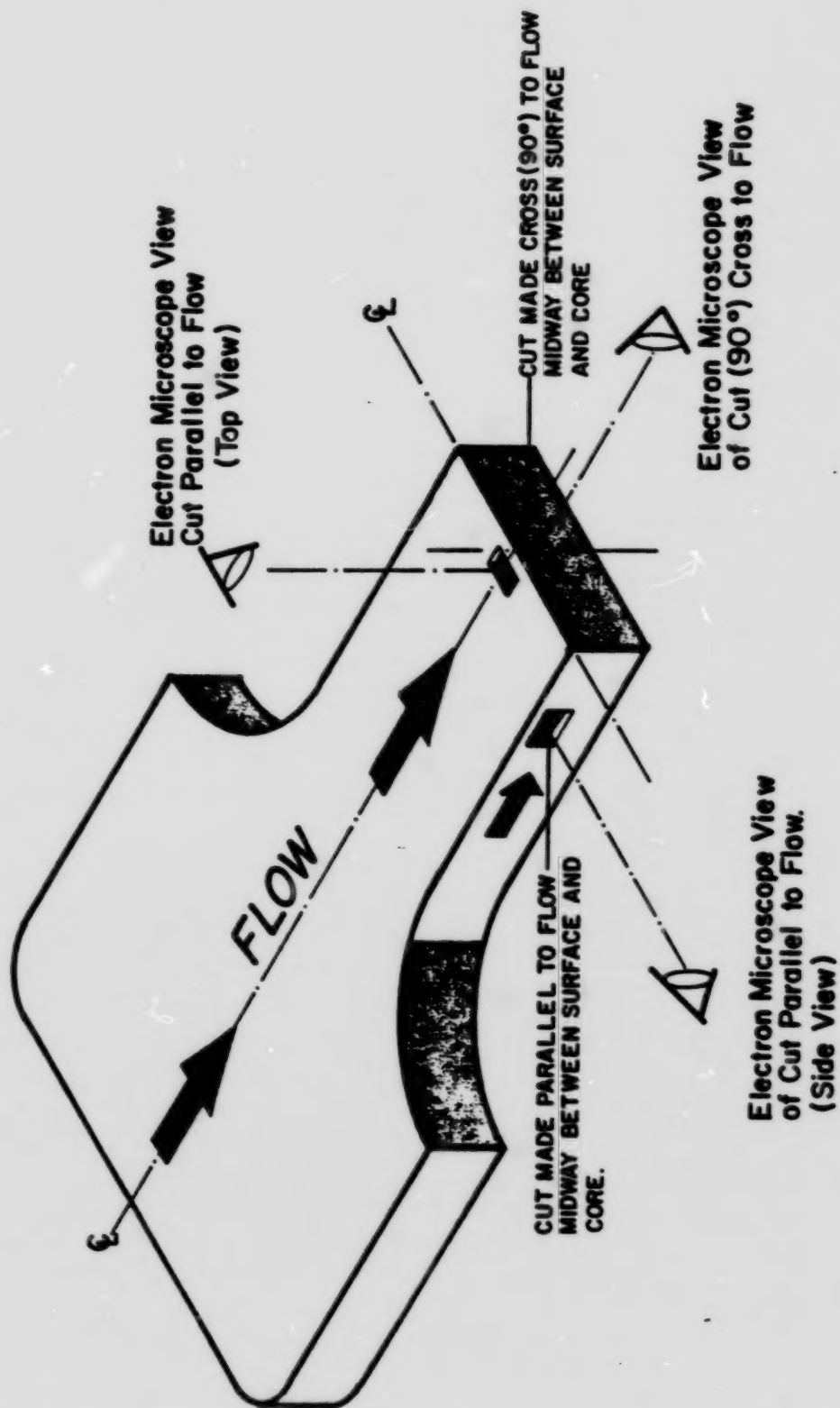


Fig. 1. Schematic of tensile bar showing areas examined by Transmission Electron Microscopy.

EXPERIMENTAL

Solvent Extraction

Pellets (2 g.) of each blend were stirred for ca. 24 hr. with 100 ml. trifluoroethanol (TFE) until the pellet disintegrated. The precipitate was separated by centrifugation and then re-extracted with 50 ml. of TFE. The combined TFE solutions were reduced to ca. 10 ml. by evaporation of the solvent under subambient pressure. This solution was then added, with rapid stirring, to ca. 100 ml. formic acid (90%). This precipitate was separated by centrifugation and the formic acid solution was reduced in volume to ca. 10 ml. This solution was then precipitated into ca. 100 ml. of methanol and the precipitate was again separated by centrifugation. The solvent was then removed from the methanol solution by evaporation under reduced pressure. The formic acid and methanol insoluble fraction were then extracted with methyl ethyl ketone (MEK) (0.5 g. solid/30 ml. MEK). All fractions were dried to constant weight under reduced pressure.

Microscopy

Samples cut from tensile bars were prepared for transmission electron microscopy using osmium tetroxide fixation followed by ultramicrotoming. Thin sections of ca. 100 nm. were collected on carbon coated grids for observation. Samples were observed in at least two mutually orthogonal directions with respect to flow for complete morphological characterization, as described in Figure 1. Surfaces of tensile bars pulled beyond their yield point were examined using standard scanning electron microscope (SEM) techniques.

Rheology

Melt Viscosity data of the four blends was obtained using a Monsanto capillary rheometer. Modulus-temperature and frequency curves were collected via Rheometrics Oscillatory Rheometer.

Physical Property Characterization

All testing was carried out using standard ASTM test methods on 3.2 mm. injection molded specimens. All specimens were molded at a 260°C stock temperature. All testing was carried out on dry, as molded, specimens. Chemical resistance to a variety of aggressive agents was measured by the method of Ruhnke(6).

Phase Separation Scheme

11/6

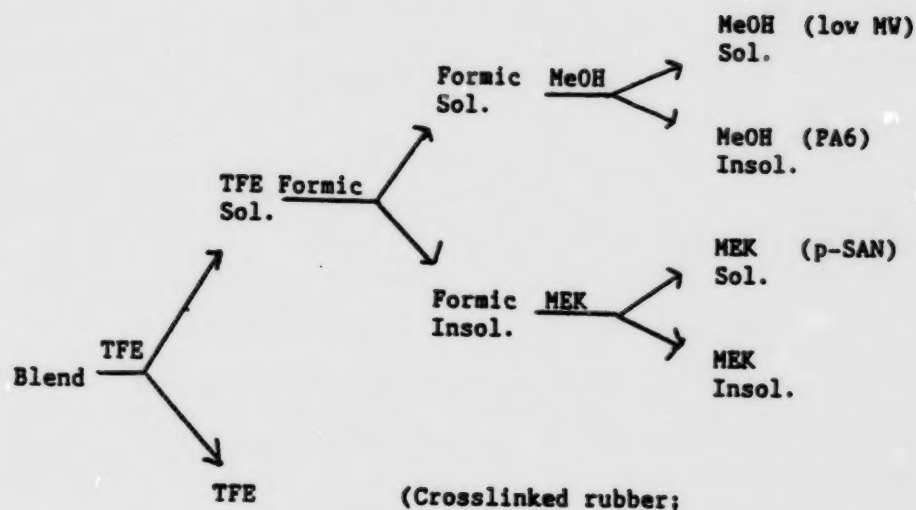


Fig. 2. Phase separation scheme.

Table I. Separation Data and IR Results

Fraction	Blend			
	A	B	C	D
TFE Ins.	ABS (32%)	PA6-ABS (34%)	ABS (34%)	PA6-ABS (35%)
TFE Sol. Formic Ins. MEK Ins.	---	PA6-ABS (4%)	PA6-SAN (4%)	PA6-SAN (4%)
TFE Sol. Formic Ins. MEK Sol.	SAN (15%)	SAN (14%)	SAN (14%)	SAN (13%)
TFE Sol. Formic Sol. MeOH Insol.	PA6 (54%)	PA6* (46%)	PA6-(SAN) (46%)	PA6-(SAN) (47%)
TFE Sol. Formic Sol. MeOH Sol.	---	SAN/PA6 Olig. (2%)	PA6 Olig. (SAN) (2%)	PA6 Olig. (SAN) (1%)

* trace PA6 grafted ABS

% Recovered normalized to 100% total recovered material

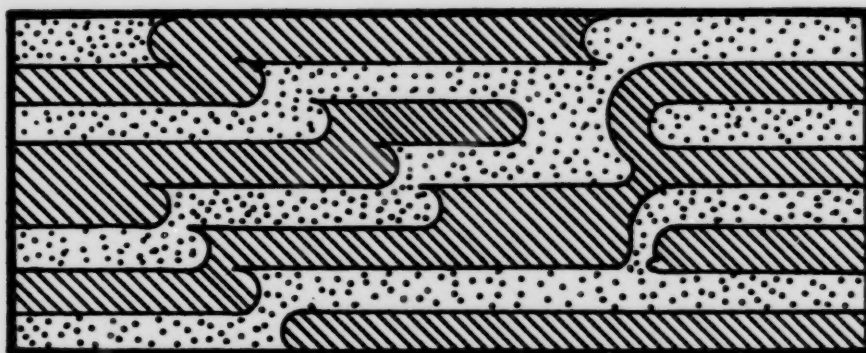


Fig. 3. Blend A cross flow view.



Fig. 4. Blend A parallel to flow (top view).

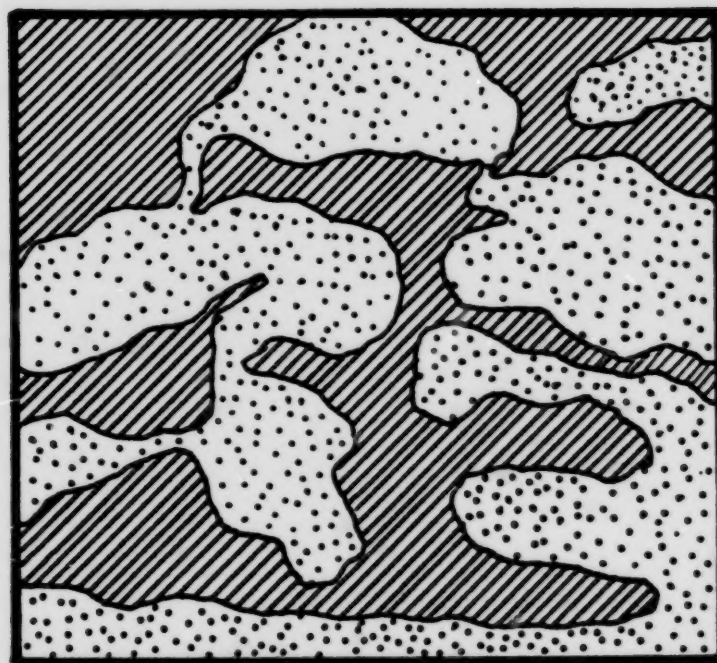
SCHEMATIC REPRESENTATION OF INTERLOCKING CO-CONTINUOUS STRATA



CROSS FLOW VIEW

 ABS

 POLYAMIDE



PARALLEL TO FLOW OR CROSS-SECTION OF STRATA VIEW

Fig. 5. Schematic of interlocking co-continuous strata.

Discussion

Solvent Extraction Studies

The solvent extraction characterization was based on the fact that both PA6 and poly(styrene-co-acrylonitrile) (p-SAN) are soluble in trifluoroethanol (TFE) while only p-SAN is soluble in methyl ethyl ketone (MEK) and only PA6 is soluble in 90% formic acid. Each blend was initially extracted with TFE to separate the insoluble, crosslinked polymer from the soluble p-SAN and PA6. The TFE solution was then precipitated into formic acid to separate the formic acid insoluble p-SAN from the formic acid soluble PA6. The formic acid solution was then precipitated into methanol. This solution was evaporated to dryness, and each fraction was extracted with MEK. The separation scheme is outlined in Figure 2.

Each fraction was characterized by infrared spectroscopy. The results of the separation and infrared studies are summarized in Table I. Blend A consists of only three components: a phase which has an infrared spectrum characteristic of an ABS, a second phase with an infrared spectrum characteristic of p-SAN, and, finally, a phase with an infrared spectrum characteristic of PA6.

The infrared analysis of the various components of Blend B suggests a different structure. The TFE insoluble fraction has an infrared spectrum characteristic of both ABS and PA6 indicating that the crosslinked, rubbery phase is grafted with PA6 as well as p-SAN. In addition, the TFE soluble/formic acid insoluble/MEK insoluble fraction has an infrared spectrum consistent with a soluble ABS which is grafted with PA6. Other components present include free p-SAN and PA6.

In Blend C the TFE insoluble phase does not contain PA6. On the other hand, soluble block or graft copolymers of p-SAN and PA6 are apparently present. In contrast to Blend B these block or graft copolymers do not contain butadiene. Finally, Blend D is similar to Blend C in that it contains soluble, butadiene free block or graft copolymer of p-SAN and PA6. In addition, the insoluble phase has infrared absorbencies characteristic of both ABS and PA6 as were found in Blend B.

Morphology

The morphology of Blend A can best be described as exhibiting a quasi-layered or stratified morphology when viewed in the cross flow and parallel to flow (top view) directions (Figures 3 and 4). The strata formed by each phase are on the order of 1 micron in breadth and extend many microns in length. Intermixing of the PA6 and ABS phases is not apparent in Blend A. The interlocking nature of the strata in these views yields a morphology of co-continuous phases. A schematic representation of interlocking co-continuous strata is shown in Figure 5.

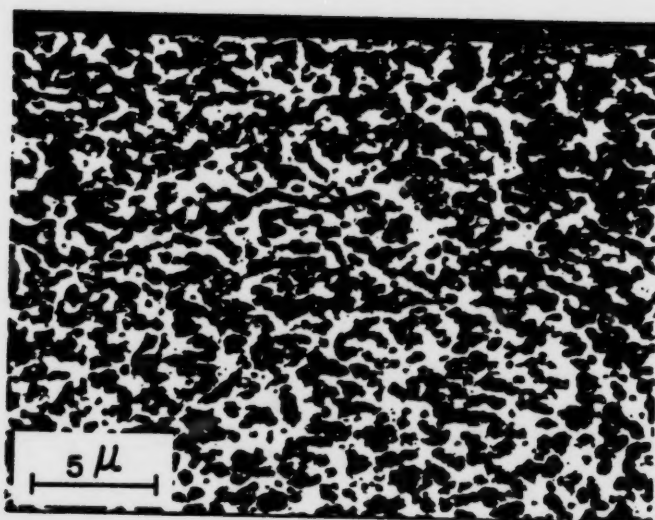


Fig. 6. Blend A parallel to flow (side view).

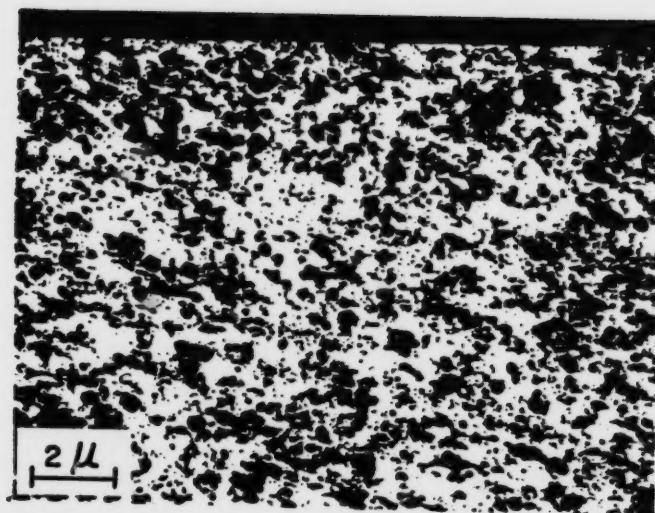


Fig. 7. Blend B cross flow view.

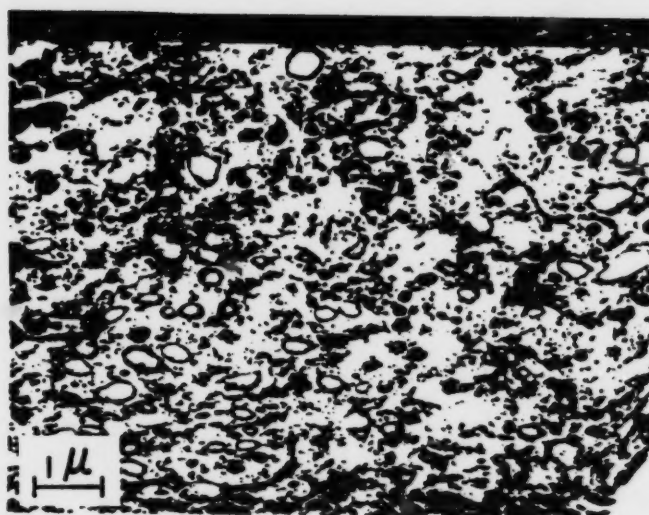


Fig. 8. Blend B parallel to flow (side view).

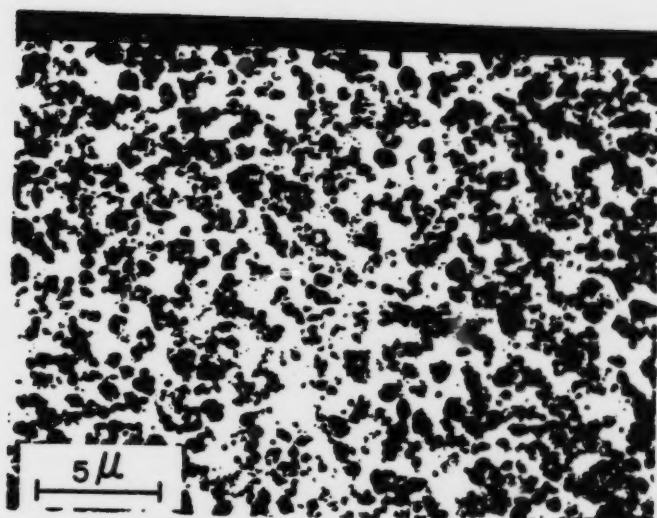


Fig. 9a. Blend C cross flow view.

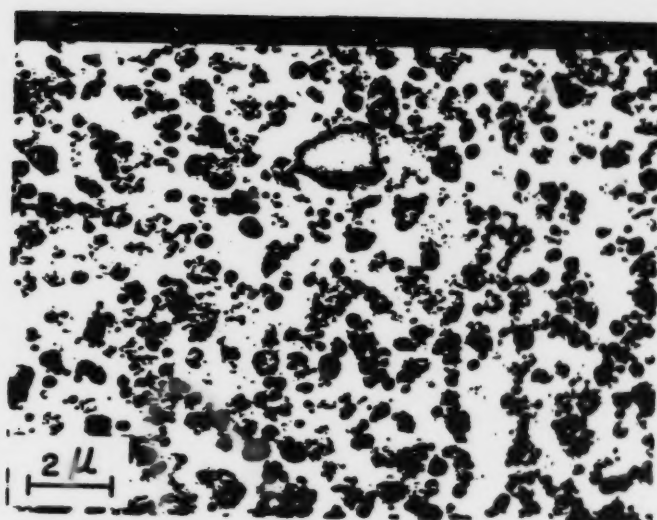


Fig. 9b. Blend C cross flow view.

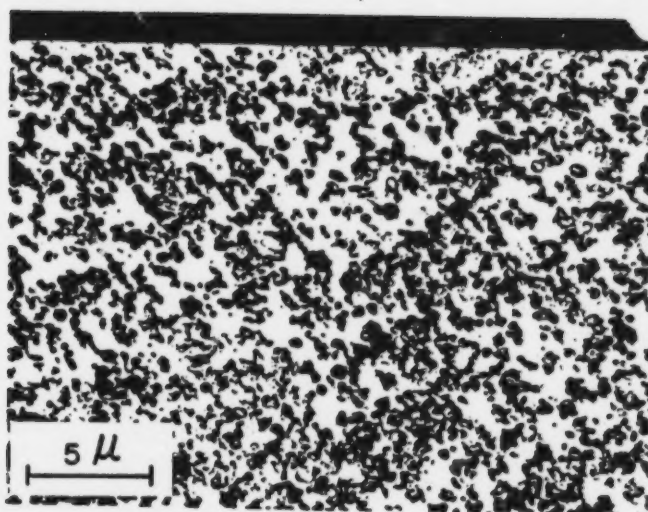


Fig. 10. Blend C parallel to flow (side view).



Fig. 11. Blend C parallel to flow (top view).

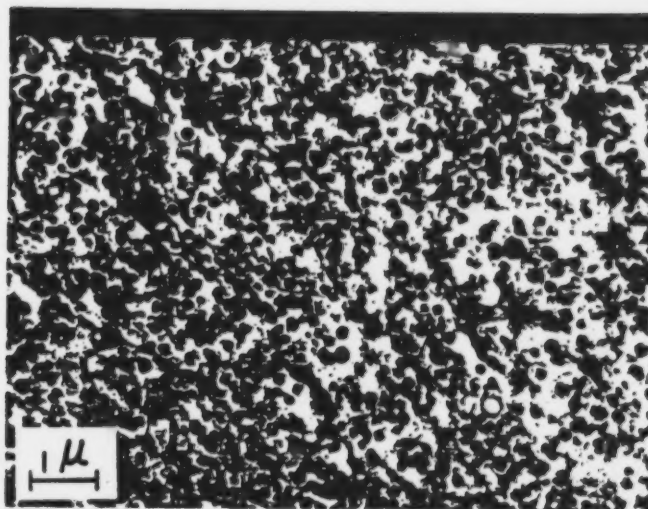


Fig. 12. Blend D cross flow view.

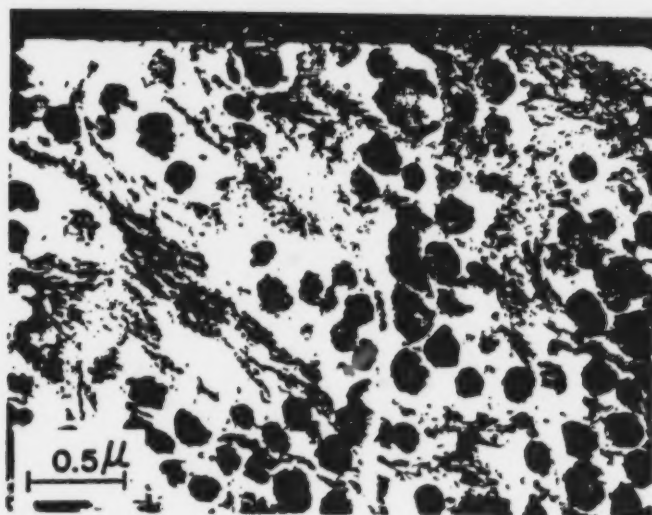


Fig. 13. Blend D parallel to flow (side view).

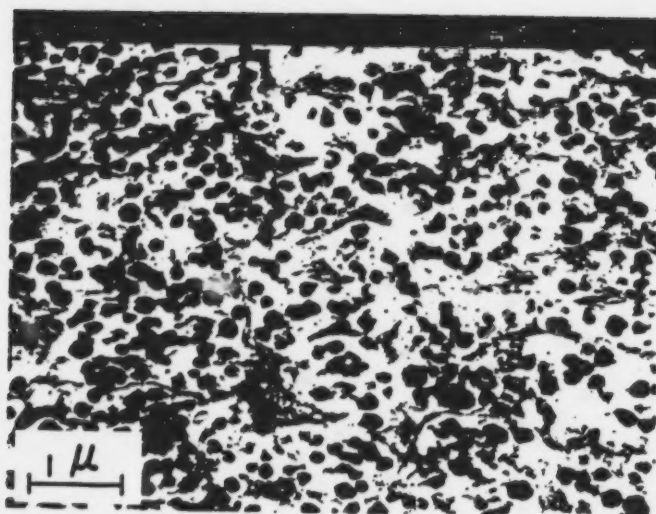


Fig. 14. Blend D parallel to flow (top view).

When Blend A is viewed parallel (side view) to flow the stratified structure becomes much less apparent (Figure 6). This view is essentially a cross-sectional view of the strata and has the form of a randomly dispersed two phase system, with PA6 seemingly the continuous phase. The phase strata are nearly two dimensional in nature with cross sections in the 1-2 microns range and the long dimension orienting itself in the cross flow direction.

The morphology of Blend B is similar in form to that of Blend A. The cross flow view, Figure 7, does show strata formation of the ABS and PA6 phases. The PA6 phase, however, has a substantial amount of the ABS dispersed within, thus making it slightly more difficult to discern the phases. The interlocking co-continuous strata structure is still the primary morphological mode of dispersion in this blend. When viewed parallel to flow (side view), Figure 8, Blend B also shows a structure consistent with that of a cross-sectional slice of a two phase, two dimensional stratified morphology. Strata dimensions are also consistent with that of Blend A.

When Blend C is examined in the cross flow direction the striated structure is no longer apparent, and the blend has the appearance of a random dispersion of an ABS phase within the PA6 phase (Figure 9a). Closer examination of the photomicrographs from this blend however, e.g., Figure 9b, indicate a co-continuous nature for both phases. The morphology parallel to flow (side view), Figure 10, is like that in the cross flow direction except the ABS phase in this case does show a preferred orientation in the flow direction although a highly stratified morphology is not formed in this dimension either. Again, based on photomicrograph examination one can argue for the co-continuousness of both phases. The parallel to flow (top view) morphology of Blend C is analogous to the parallel (sideview) structure in that the ABS phase tends to be oriented in the direction of flow, (Figure 11). The phases in this blend are more ribbon like than droplets or fibrils.

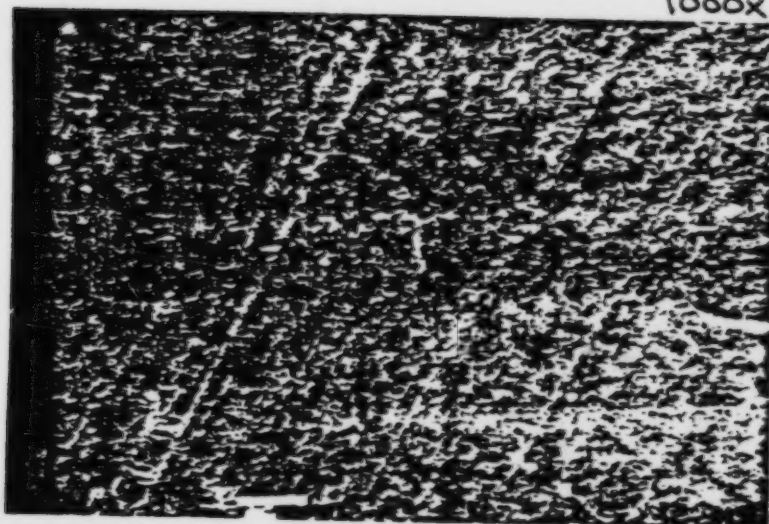
Blend D exhibits a unique morphology in that its structure remains the same when observed in the mutually orthogonal directions to flow. Figure 12 shows the cross flow morphology while Figures 13 and 14 show the parallel to flow (side and top view), respectively. The ABS phase of this blend is dispersed in a continuous PA6 phase. Morphologies such as these are referred to as cellular (7,8), meaning one phase occupies the "cell" space and the other phase forms the continuous membrane encapsulating the cells.

Both polymer structure and morphology are known to influence the deformation mechanism of a material under the influence of external forces(9). Two blends, A & D, representing the extremes in morphologies characterized in this work were examined for deformation process after pulling the bars in tension beyond their yield point.

1700x



1000x



Figs. 15a,b Blend A, yielded tensile bar surface.

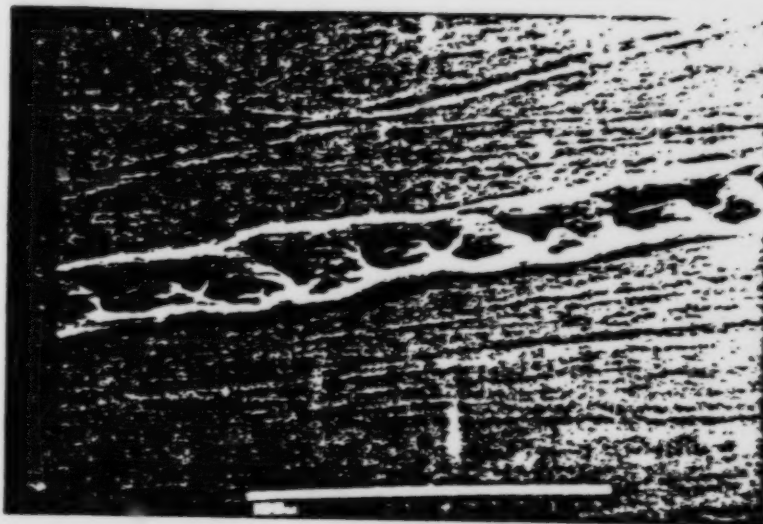


Fig. 16a,b Blend D, yielded tensile bar surface.

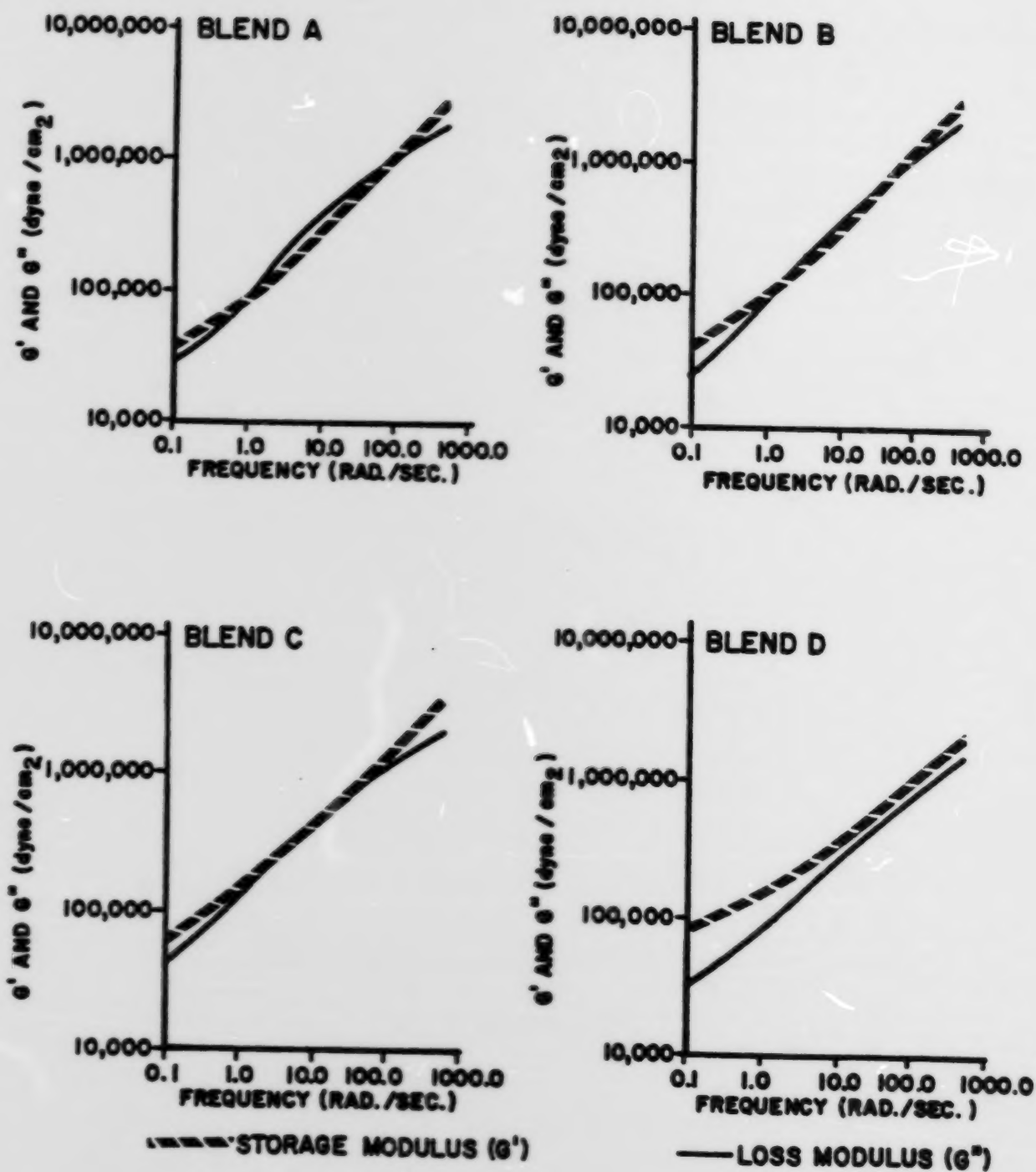


Fig. 17. Shear moduli-frequency curves for Blends A, B, C, and D.

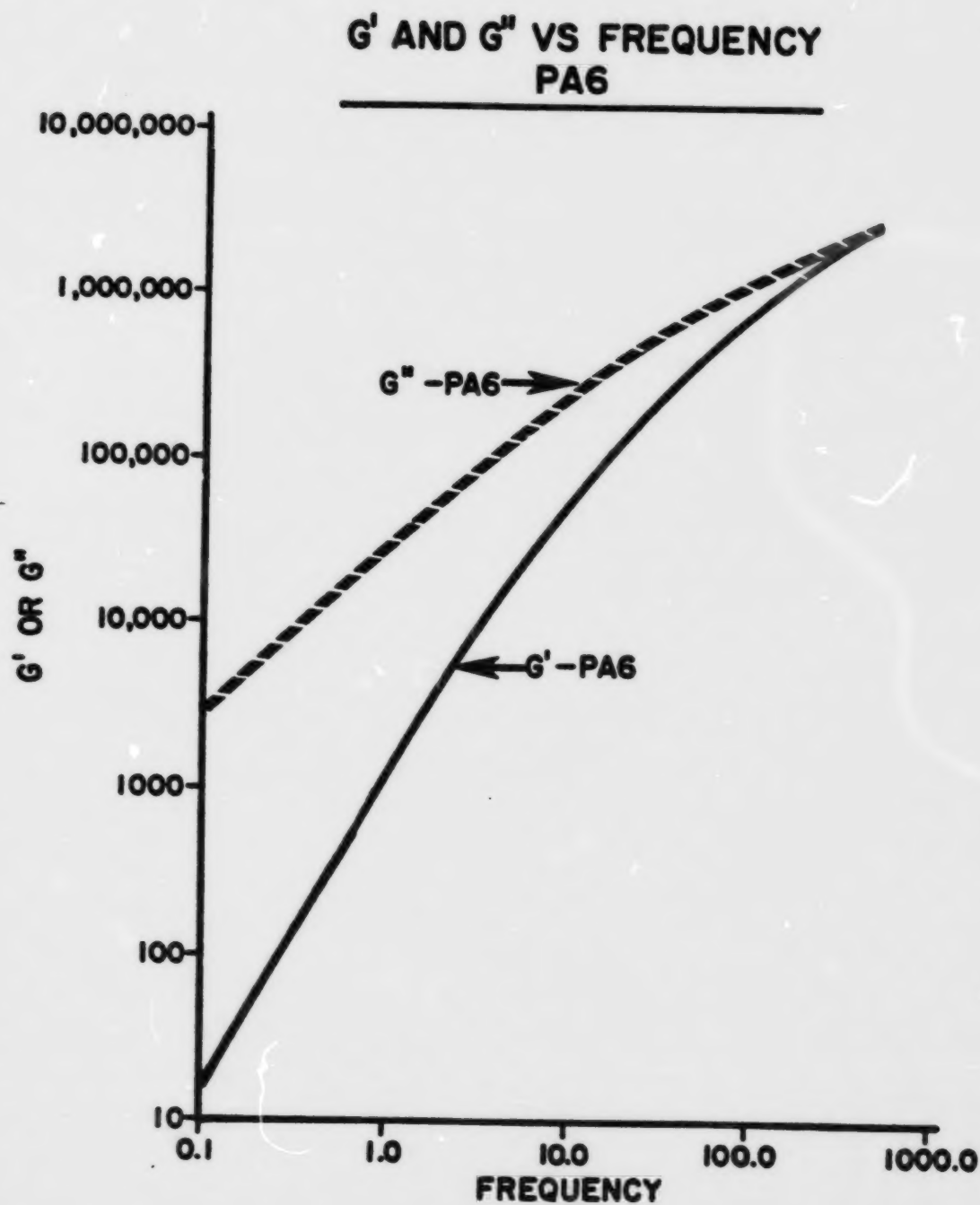


Fig. 18. Shear moduli-frequency curve for PA6.

STORAGE MODULUS VS TEMPERATURE

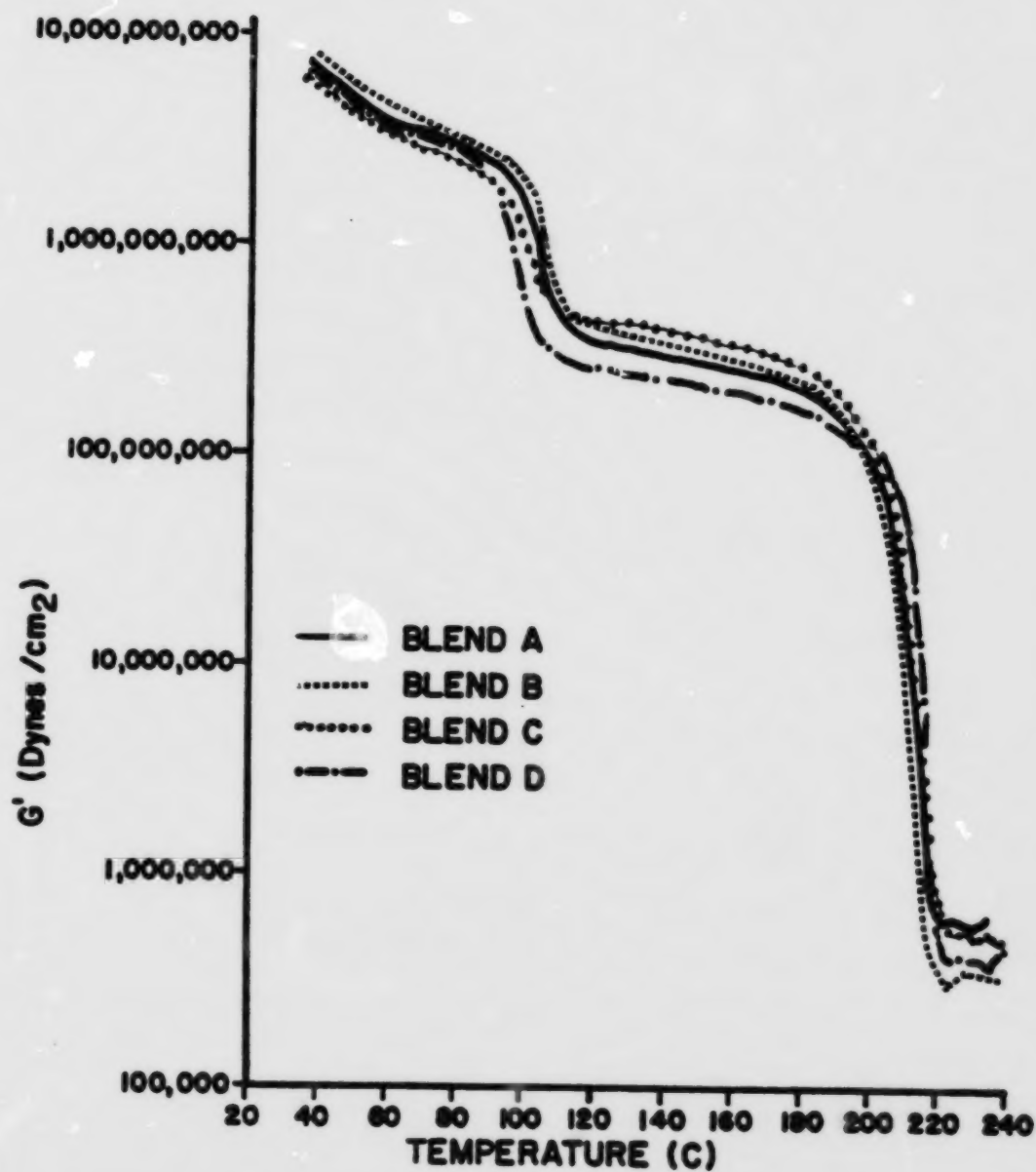


Fig. 19. Shear moduli-temperature curves for Blend A, B, C, and D.

Table II. Physical Properties of Blends

IMPACT STRENGTH

	BLEND A	BLEND B	BLEND C	BLEND D
IZOD IMPACT (3.175 mm IM) (J/m)				
RT	896	891	897	864
10°C	112	240	165	234

INSTRUMENTED DART (DYNATUPTM) IMPACT (3.175 mm IM DISKS)

RT				
TOT. ENERGY (J)	73.0	62.0	72.8	58.9
DUCT./BRITTLE	5/0	3/0	5/0	5/0
-29°C				
TOT. ENERGY (J)	58.6	18.4	60.2	36.7
DUCT./BRITTLE	4/0	1/2	3/1	3/2

TENSILE

YIELD STRENGTH (MPa)	49.9	50.5	49.7	41.4
BREAK STRENGTH (MPa)	42.7	46.2	48.4	----
MODULUS (GPa)	2.2	2.5	2.2	2.0
ELONGATION (%)	176	213	259	166

HEAT DISTORTION PROPERTIES

HEAT DISTORTION (°C) (3.175 mm, 455KPa)	96	----	93	88
--	----	------	----	----

MELT VISCOSITY @ 260°C (poise)

Shear rate				
100 sec-1	12130	10632	11410	9694
1000 sec-1	2680	2925	2770	2524

CHEMICAL RESISTANCE	EXCELLENT	EXCELLENT	EXCELLENT	EXCELLENT
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Typically rubber modified systems, e.g., HIPS, ABS, etc., deform via a craze forming mechanism while semi-crystalline polymers, e.g., PE, PP, polyamides, etc., deform via a shear banding mechanism(10). SEM examination of yielded surfaces show that Blend A (Figure 15a and b) deforms primarily through a crazing mechanism as evidenced by the voids opened on the surface and extended perpendicular to the stress direction although the crazing may be preceded by a shear mechanism. Blend D deforms through a shear banding process as indicated by bands of oriented material aligned at ca. 45° with respect to the stress direction (diamond shaped pattern, Figure 16a and b).

Rheology

Capillary melt viscosity data at 245°C for two shear rates is shown in Table II. The maximum spread in viscosity at the low shear rate among the four blends is 20%, and the viscosity differences typically decrease as shear rate increases. Shear moduli-frequency data for the four blends are shown in Figures 17a, b, c, and d. Blends A, B, and C show very similar behavior. Blend D differs somewhat in that the storage modulus (G') is greater than the loss modulus across the entire frequency range.

The differences in rheological behavior could arise in part from the observed morphological and structural differences among the blends. In particular, the fact that morphology of Blend D consists of a disperse ABS phase in a PA6 continuum may partly account for the separation between the G' and G'' vs. frequency curves of this blend since these curves are separately in pure PA6 (Figure 18). The overall shapes of the curves for Blend D are, however, similar to those of Blend A - C. Uncharacterized factors such as blend to blend variations in the molecular weights and molecular weight distributions of the various polymeric components may be more significant.

Shear moduli-temperature data for the four blends show extremely similar behavior despite the variety of structure and form. The general nature of these curves (Figure 19) indicates that the shear modulus of the blend is reinforced by the p-SAN phase in the region between the T_g of the PA6 phase ($\sim 40^\circ\text{C}$) and that of the p-SAN phase ($\sim 105^\circ\text{C}$). At temperatures above the T_g of the p-SAN phase the modulus decreases to a level where the blend is now reinforced by the presence of the semi-crystalline PA6 phase. The final drop in modulus then occurs at the PA6 melt temperature ($\sim 220^\circ\text{C}$).

Physical Properties

Physical property data including impact strength (Izod and instrumented dart) tensile properties, heat distortion temperatures, and chemical resistance are given in Table II. These are quite similar for the four blends. Blend D has slightly lower tensile properties and heat distortion temperature than the other three blends. This is consistent with the modulus-temperature curves (Figure 19).

The similarity in impact strengths for the four blends is perhaps the most surprising observation. The room temperature Izod impact and instrumented dart impacts have similar values for all four. Although there is a somewhat greater difference in the absolute values of the low temperature impact strength, the ductile/brittle transitions temperatures for all four are similar. These four blends with differing morphologies, polymer micro-structures, and deformation mechanisms have very similar impact strengths when measured under a variety of test conditions.

CONCLUSIONS

The extractions studies indicate that different kinds of compatibilization structures are present in these four blends. In Blend A, the interfacial energy is sufficiently low between the ABS and PA6 phases that no graft structures are required. On the other hand, Blends B, C, and D all contain p-SAN or ABS grafted with PA6. Blend B contains ABS grafted with PA6, Blend C contains p-SAN grafted with PA6, and Blend D contains both types of graft structures.

The morphologies of the materials examined can be placed into three general categories: stratified (Blends A & B), droplet/ribbon (Blend C), and cellular (Blend D). The structure of the blend components appears to influence the morphological form to some degree although other variables may be important. For example, those blends (B and D) which have ABS dispersed in the PA6 phase contain ABS grafted with PA6.

Rheological characteristics of the blends are very similar especially considering the range of morphologies and structures comprising the blends. Differences in unmeasured variables such as molecular weights and molecular weight distributions could readily account for the differences.

The conventional physical properties are also remarkably similar considering the range of structures. All blends share the same reinforcement phenomena of p-SAN and PA6 over the shear modulus-temperature range studied and display similar impact properties. The data indicate that the physical properties of these systems are much more dependent on the fundamental properties of the ABS and PA6 components than the precise manner in which these components are combined into the blend.

ACKNOWLEDGMENT

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THE EFFECT OF VISCOSITY RATIO ON THE MORPHOLOGY OF
POLYPROPYLENE/POLYCARBONATE BLENDS
DURING PROCESSING

by

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ABSTRACT

The size of the minor phase in an immiscible polymer blend can have a significant effect on properties such as the impact strength. Few studies, however, have quantitatively considered the parameters controlling the size of the dispersed phase. In this paper light and scanning electron microscopy have been used to examine the size of the minor phase in polypropylene/polycarbonate blends after melt processing. The size was examined as a function of both the viscosity ratio (p) and the torque ratio (TR). The viscosity ratio is studied in the regions of $p > 1$ and $p < 1$. p has a marked effect on the morphology of the dispersed phase with the phase size increasing by a factor of 3-4 times from $p = 4.5$ to $p = 17.3$. Significant deformation of the minor phase was achieved below $p = 1$ with the minimum particle size occurring at $p = 0.15$. The results for these systems indicate the presence of an upper and lower limit of p beyond which deformation becomes difficult. This is shown to be similar in some respects to the behavior of Newtonian fluids in shear flow.

INTRODUCTION

The minor phase in an immiscible polymer blend is deformable as opposed to composite materials which contain a rigid minor phase. A wide range of sizes and shapes can thus be obtained for this dispersed phase during processing. Generally the sizes range from about $0.1\mu\text{m}$ to $20\mu\text{m}$ and spherical, ellipsoidal, cylindrical, and ribbon-like morphologies may be prepared. Control of the morphology of immiscible blends during processing is of critical importance but, as yet, remains a poorly understood phenomenon.

The melt rheology of a system is particularly sensitive to morphology [1,2]. Han and Kim [1] in studying PS/PP blends found that even moderately different modes of dispersion and particle size can give rise to pronounced differences in the apparent rheological properties in the molten state. Significant differences in plots of the first normal stress difference versus composition were observed for materials prepared in a single screw extruder equipped with a Koch static mixer compared to samples prepared in a twin screw extruder.

Control of the morphology, that is to say the size and distribution of the minor phase, has a profound influence on the mechanical properties, especially impact strength.

Impact energy may be dissipated by two main mechanisms [3]. Type I polymers which are brittle (e.g. polymethylmethacrylate, polystyrene) dissipate energy through crazing. Type II polymers which are ductile (e.g. polypropylene, nylon, polycarbonate) undergo shear yielding as their main

fracture mechanism. Rubber toughening for the former occurs through increased matrix crazing while for type II polymers the addition of rubber allows for increased matrix yielding. For type I polymers there exists an optimum particle size of the rubber particle for maximum toughness. For type II polymers a sharp tough to brittle transition can occur at a critical particle size. For example, in 15% rubber/nylon blends a fourfold drop in the notched Izod impact strength was observed in increasing the number average particle size from $0.7\mu\text{m}$ to $0.8\mu\text{m}$ [4]. At 25% by weight of a rubber/nylon blend, a fourfold drop was similarly observed from $1.5\mu\text{m}$ to $2\mu\text{m}$. Recent studies [4] for these systems indicate that it is predominantly a critical surface to surface interparticle distance which determines toughness. Asar [5] observed in EPDM/PP blends that local variations in EPDM concentration and domain sizes can result in a twofold difference in the total energy absorbed during impact.

The shape of the minor phase is also of critical importance. Deformation of the minor phase in the direction of extrusion can significantly improve the elongation at break in the machine direction [6], even in the absence of chemical compatibilization. Another novel example of the importance of shape in immiscible blends is illustrated in DuPont's Selar[®] technology (nylon/HDPE/ionomer) where the minor phase in the form of platelets can result in a significant improvement in barrier properties with respect to hydrocarbons [7,8].

Several basic parameters are important to consider in controlling particle deformation. They are briefly: composition, viscosity ratio, shear stress/shear rate, interfacial tension and elasticity.

Avgeropolous [9] has shown by transmission electron microscopy that for a variety of compositions and torque ratios for an EPDM/BR blend the smallest domains are obtained when the mixing viscosities of the components are equal. He found that the particle size in these systems increases with the ratio of mixing viscosities of the components (calculated as torque ratio).

Van Oene [10] has studied the effect of both viscosity and elasticity and has shown that the elastic contribution to the interfacial tension can result in the tendency for a phase of high elasticity to encapsulate one of low elasticity. He indicates that it is generally difficult to deform a highly elastic material.

Min et al. [11] noted that for PE/PS the scale of the phase morphology was made much finer by shearing at high shear stresses. The scale of the morphology with PE/PS was shown to be independent of the mixing temperature from 180°C to 240°C and polyethylene molecular weight even though these variations would be expected to influence the viscosity ratio. In studying polyethylene/polystyrene, polyethylene/polycarbonate, polyethylene/nylon-6 and polypropylene/nylon-6 prepared in the same manner with a single screw extruder and a Koch static mixer these authors found that the finest phase morphology was found with the PE/PS and the coarsest with PE/nylon-6 and PP/nylon-6 [12].

Wu [13] shows for nylon/rubber systems that viscoelastic drops can breakup during extrusion even when the viscosity ratio, η (viscosity of dispersed phase/viscosity of the matrix), is greater than 4. He suggests that

as the viscosity ratio increases above unity or decreases below unity the dispersed particles become larger. He also found that the decrease in the dimensions of the minor phase of a chemically modified rubber system compared to the unmodified case were significant and closely related to the decrease in interfacial tension.

In a previous publication [14] the dependence of the size of the minor phase on composition was studied for polypropylene/polycarbonate blends. Two blend systems of significantly different viscosity ratios were studied over the entire composition range. It was shown that the viscosity ratio has a significant effect on the phase size/composition relationship and that there was a shift in the composition at which dual phase continuity was observed. The position of phase inversion as determined by morphological examination was found to correspond to the same concentration where a sudden increase in the torque of the blend system was observed.

In light of the close relationship between blend morphology and the mechanical and physical properties of the system, it is very important to understand the factors controlling the morphology of polymer blends during processing. It is especially critical in studies of this type that the virgin materials be well characterized, especially for their rheological functions, and that the morphological techniques used in analyzing the blends be well described. The previous study described above focused predominantly on the effect of composition on phase size. In this paper we will examine in detail the effect of the viscosity ratio (above and below unity) on the size of the minor phase for polypropylene/polycarbonate blends.

DROPLET BREAKUP

Einstein [15] developed the expression for the viscosity of a fluid containing solid spheres in suspension. This theory was later extended by Taylor to consider the case of the spheres being liquid. In studying Newtonian liquids suspended in another Newtonian liquid Taylor [16-18] observed that when the radius of the drop was great enough or when the rate of distortion was high, the drops break up. He developed Eq. (1) which is an expression for determining the size of the largest drop which exists in a fluid undergoing distortion at any rate.

$$a = \frac{2T(\eta_d + \eta_m)}{\alpha \eta_m \left(\frac{19}{4} \eta_d + 4\eta_m \right)} \quad (1)$$

where a = radius of drop, T = surface tension, α = parameter related to the shear rate, η_m = viscosity of matrix, η_d = viscosity of dispersed phase.

The shape of the drop can be determined by Eq. (2):

$$D = (L-B)/(L+B) \quad (2)$$

where L is the greatest length and B is the width.

Two basic conditions of flow were studied by Taylor: uniform shear flow using a parallel band apparatus and hyperbolic or extensional flow using a four roller apparatus. The basic principle of droplet deformation is that as

soon as the disruptive stress due to the viscous drag of the medium is able to overcome the cohesive effect of surface tension, the drop bursts.

The act of bursting involves elongation to a thin cylindrical form which breaks up into aligned drops of the order of 1/100 of the size of the original drop. Hence, throughout the system drops are obtained which cover a very large range of sizes.

At high viscosity ratio ($p = 20$) it was found that the drop still burst in the hyperbolic flow field whereas in uniform shear flow the drop would not burst even at the highest possible speeds. Karam and Bellinger [19] and Tavgaç [20] have studied the breakup of Newtonian droplets in a Newtonian matrix over a wide range of viscosity ratios in uniform shear flow. Their results describe a U-type dependence of droplet breakup with viscosity ratio which indicates that there is an upper and lower limit of viscosity ratio beyond which no breakup occurs. Karam and Bellinger report that in uniform shearing flow droplet breakup would occur within $0.005 \leq p \leq 3.0$. Tavgaç reported the range as $0.0033 \leq p \leq 3.7$. At high viscosity ratios the viscous forces which disrupt the drop could not overcome the interfacial forces which keep it together, whereas at very low viscosity ratios the drop was highly deformed, but did not break. An extensional flow field is found to be much more effective for breaking up droplets and the limiting viscosity ratio range is much greater than that for uniform shearing flow. Taylor defined a dimensionless parameter E which represents the ratio of viscous to surface tension forces. E may be expressed as:

Table 1 CHARACTERIZATION OF POLYCARBONATE AND POLYPROPYLENE MATERIALS

	Melt Index (ASTM) g/10 min	Density at 250°C (g/cc)	Torque 5 min mixing 250°C	η' at 100rad/ sec (Pa·sec)	$\bar{M}_n$	$\bar{M}_w$
POLYCARBONATE						
(M-39) PC-1	18	1.08	26.9	1.79×10^3	12,300	26,500
(M-40) PC-2	9	1.08	37.6	2.19×10^3	13,200	30,300
(M-50) PC-3	4.5	1.08	49.8	2.76×10^3	16,500	36,300
POLYPROPYLENE						
(6301) PP-1	12	0.75	3.9	1.60×10^2	31,300	200,000
(6501) PP-2	4	0.75	6.7	2.48×10^2	50,000	325,000
(6701) PP-3	0.8	0.75	12.7	3.93×10^2	72,000	470,000

$$E = We [(19p+16)/(16p+16)] \quad (3)$$

where p is the viscosity ratio of the droplet phase to the suspending medium.

"We" may be expressed as:

$$We = \eta_m a \dot{\gamma} / \sigma \quad (4)$$

where " η_m " represents the viscosity of the matrix, " a " represents the radius of the droplet, $\dot{\gamma}$, the rate of shear and " σ " the interfacial tension. Droplet breakup occurs at a critical value E_c . If $We > (We)_c$, the droplet will deform and break.

EXPERIMENTAL

(1) MATERIALS. Three commercial grades of polycarbonate and three of polypropylene were examined in this study. The polycarbonates are Merlon M-39, M-40, and M-50 obtained from the Mobay Corporation and are derived from bisphenol-A. The polypropylene samples are Pro-Fax 6301, 6501 and 6701 obtained from Hercules. Their properties, including the number average and weight average molecular weights [21,22], are summarized in Table 1. Throughout this paper polycarbonates M-39, M-40 and M-50 will be referred to as PC-1, PC-2 and PC-3 respectively. Polypropylene 6301, 6501 and 6701 will be referred as PP-1, PP-2 and PP-3 respectively. Various combinations of PC in PP allowed the study of the viscosity ratio in the range of $p > 1$. Inversion of the phases (PP in PC) allowed the study of the $p < 1$ region.

(ii) MIXING.

Prior to a typical mixing experiment the sample mixture was dried for 17 hours under vacuum at 90°C in order to minimize hydrolytic degradation of the polycarbonate during processing. The polypropylene was stabilized with 0.2% antioxidant. The materials were then melt blended in a Brabender mixing chamber using the roller blade attachment normally used for viscous materials and the experiments were carried out under dry nitrogen. The volume of the material in the chamber was kept constant at 60 ml (calculated at 250°C) and the densities of polycarbonate and polypropylene at 250°C were 1.08 and 0.75 g/cc respectively [4, 5]. Blending conditions were maintained at 250°C and 50 rpm for 5 minutes. A temperature of 250°C was chosen deliberately in order to minimize the thermal degradation of polypropylene. After blending, the melt was rapidly shaped into a block and cooled in ice water. The samples were stored at -25°C to eliminate any long term morphological change with time.

iii) MORPHOLOGICAL ANALYSIS.

Optical Microscopy - Polypropylene-rich samples for light microscopy were microtomed, extracted with methylene chloride to etch the polycarbonate, immersed in oil, and then photographed with high contrast film under bright field conditions. The microscope used was a Leitz/Wetzlar, Dialux 20.

Electron Microscopy - A scanning electron microscope (type JEOL 35 CF) was used to examine the polycarbonate-rich samples since the disperse phase tended to be of smaller size. The samples were microtomed to create a plane face using an ultramicrotome (Reichert-Jung Ultracut) equipped with a glass knife. The samples were then subjected to decalin at 130°C for 15 minutes in order to

dissolve the minor phase. Since the microtome does not necessarily cut the dispersed sphere at the widest point, a correction was applied in order to obtain the true diameter [4].

Image Analysis - A semi-automatic method of image analysis was used to quantify the size of the minor phase. It consists of a unidirectional digitizing device that works as follows: as the crosshair of a magnifier connected to the mobile part of a linear variable differential transformer (LVDT) is moved over the photomicrograph, the Ferrets diameter of a domain is recorded and stored in a microcomputer for the calculation of statistical parameters. Four fields of view and 200 diameters are considered for a given sample. The number average diameter, d_n ; the volume average diameter (also known as the moment mean diameter), d_v ; and full distribution curve were obtained in this way. Increasing the number of measurements to 400 or 600 did not significantly alter the results. The average error in the reported diameters is ~10%.

iv) RHEOLOGICAL ANALYSIS.

The Rheometrics Mechanical Spectrometer, RMS, Model 605, was used to measure the dynamic viscosity, η' , and the storage modulus, G' , as a function of frequency at 250°C. The experiments were carried out in the dynamic mode in parallel plate geometry at a strain of 10% and gap of 1.2 mm. The experiments were performed under a dry nitrogen blanket.

The torque values reported in the text were measured in the mixing chamber at 250°C and at about 5 minutes mixing. Values for the pure materials

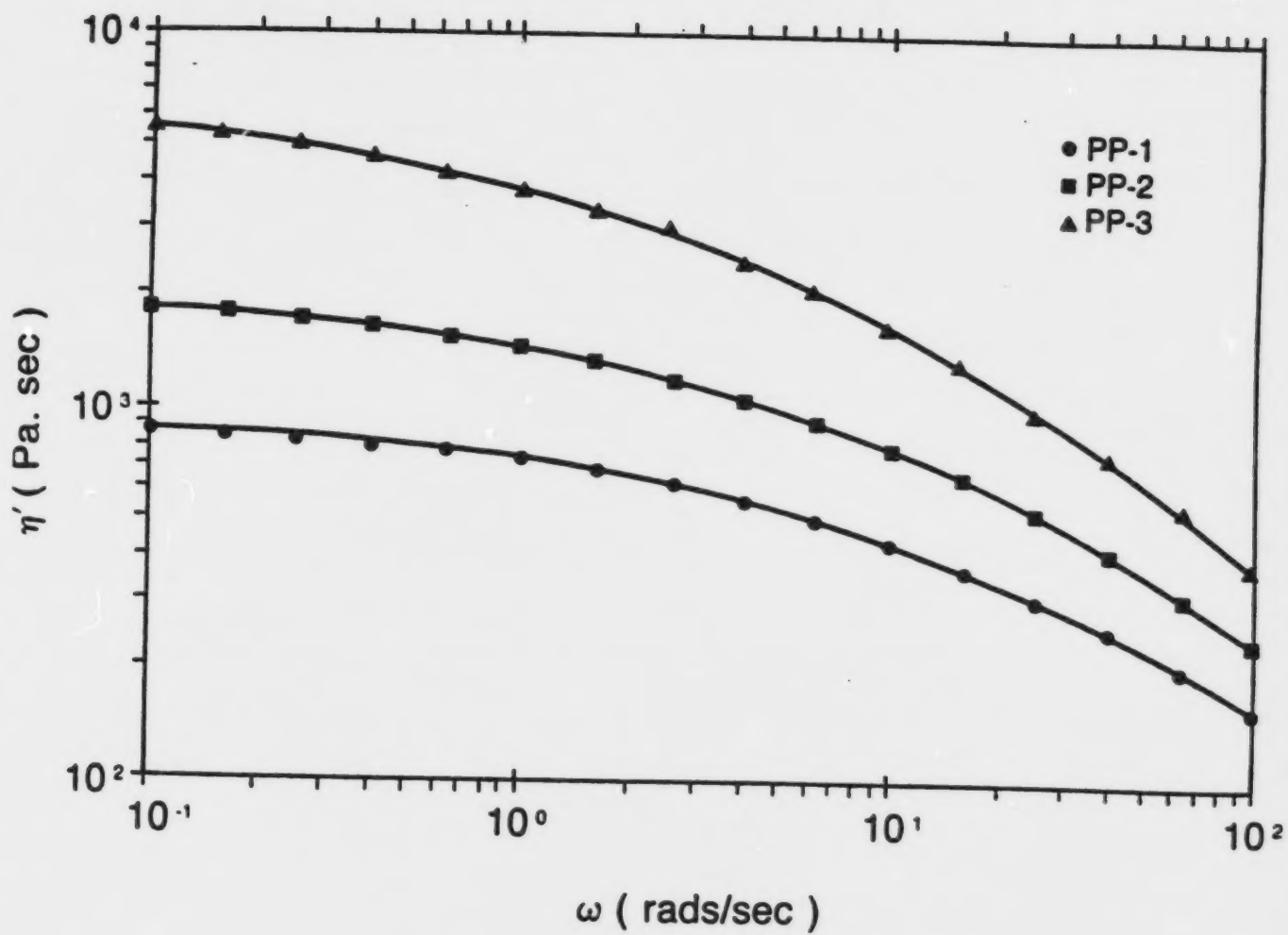


Fig. 1 η' versus ω for the three virgin polypropylene samples at 250°C.

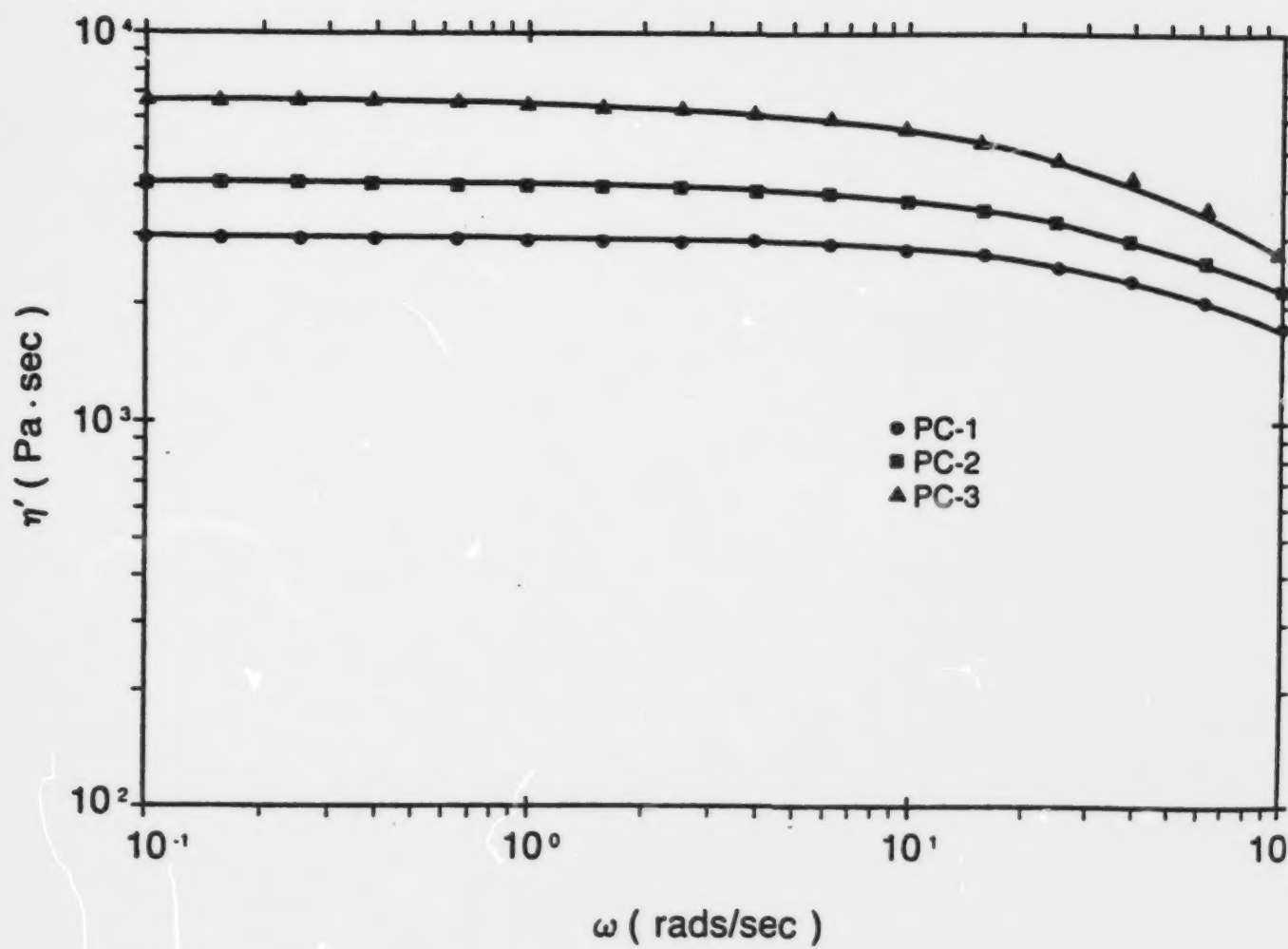


Fig. 2 η' versus ω for the three virgin polycarbonate samples at 250°C.

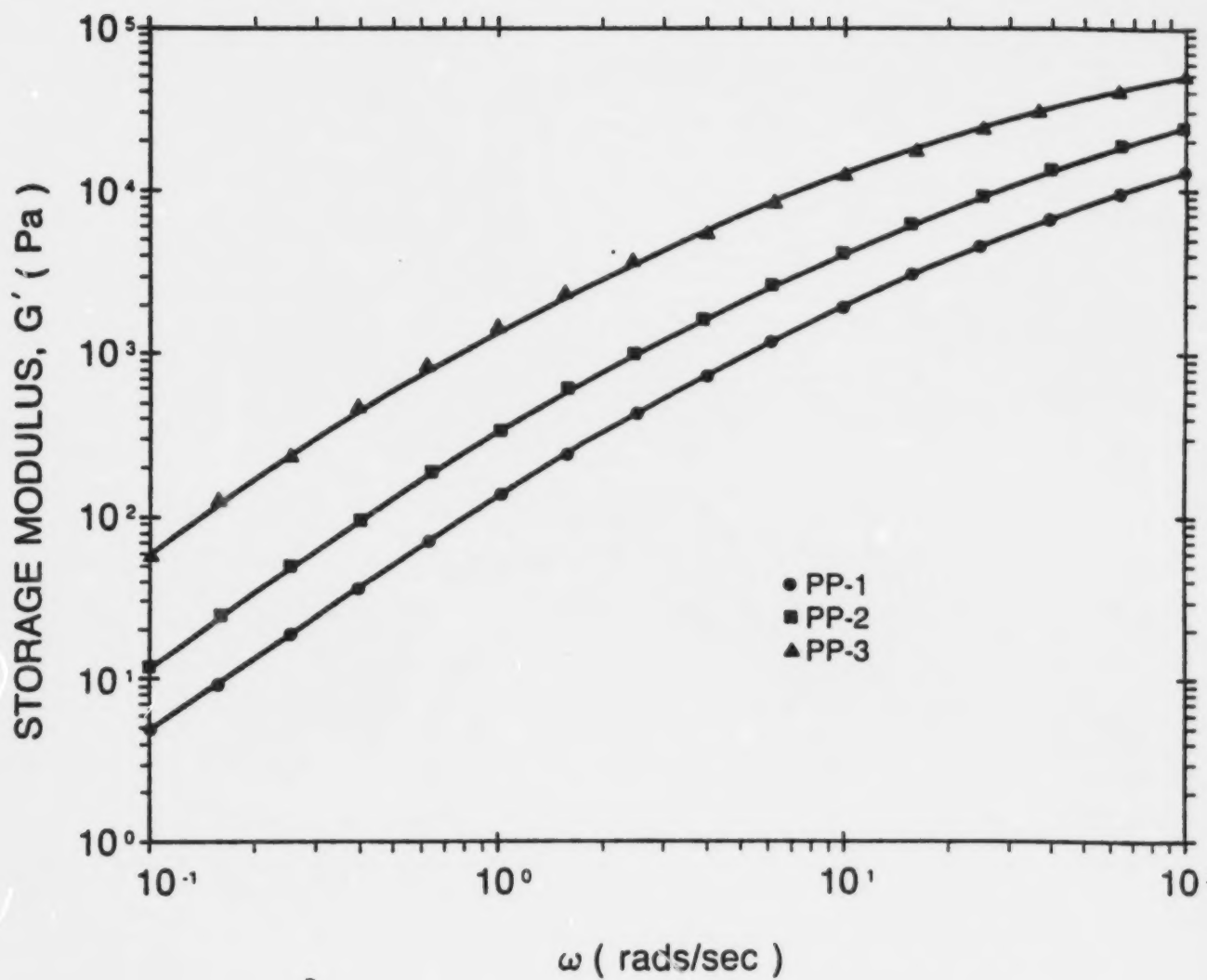


Fig. 3 G' versus ω for the three virgin polypropylene samples at 250°C.

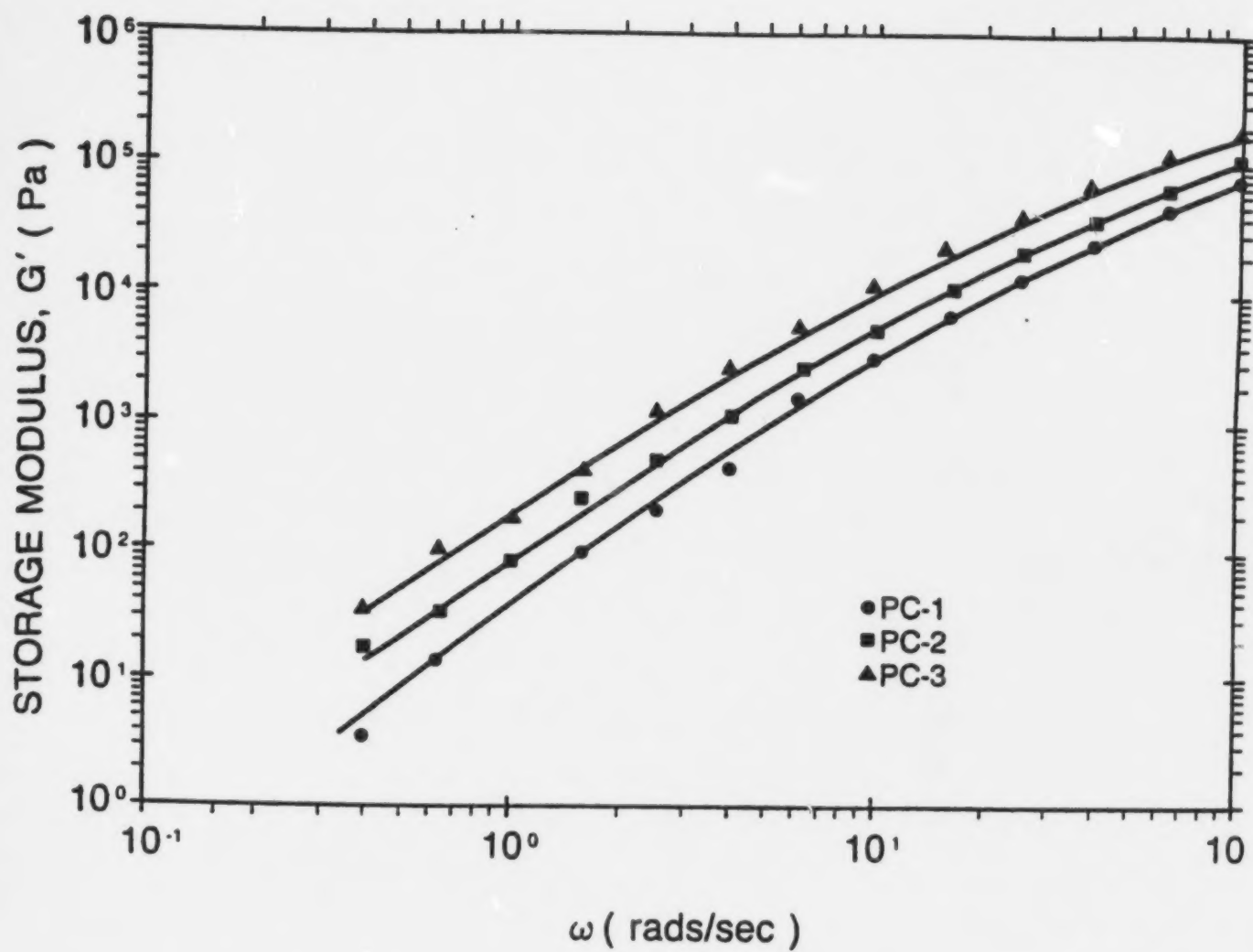


Fig. 4 G' versus ω for the three virgin polycarbonate samples at 250°C.

are given in Table 1. PC-2 and PC-3 were found to be sensitive to shear degradation when processed for long periods such as 15 or 20 minutes. Hence the samples were mixed for 5 minutes in order to minimize this effect. A comparison of several samples showed the equilibrium torque ratio to be very similar to the torque ratio at 5 minutes.

RESULTS AND DISCUSSION

In Figure 1 the dynamic viscosity versus shear rate is plotted for the three commercial polypropylene samples at 250°C. Figure 2 shows a similar plot for the polycarbonate samples. The polycarbonates exhibit high viscosity and long plateau-like behavior over a wide range of frequency indicating little shear sensitivity. This behavior, is well documented for polycarbonates whose high viscosities have been attributed to the small mobility of the molecular chains caused by the hindered rotation of the aryl nuclei [23]. It can be seen that the polypropylene samples cover a 2.4-fold range of viscosity at 100 rad/sec while the polycarbonates cover a 1.6 fold range at the same frequency. Various combinations of the polypropylene/polycarbonate samples allow the study of viscosity ratio in the range of $p > 1$, from ~ 4 to 17 when polypropylene is the matrix. Inversion of matrix and dispersed phase allows the study of phase size versus viscosity ratio at $p < 1$, from p of 0.06 to 0.25.

Figures 3 and 4 show the dependence of the elastic storage modulus versus frequency. At 100 rad/sec, which is close to the shear rate of 185 s^{-1} calculated for the mixing chamber, polycarbonate is in all cases more elastic than polypropylene. In fact, close observation indicates that the elasticity

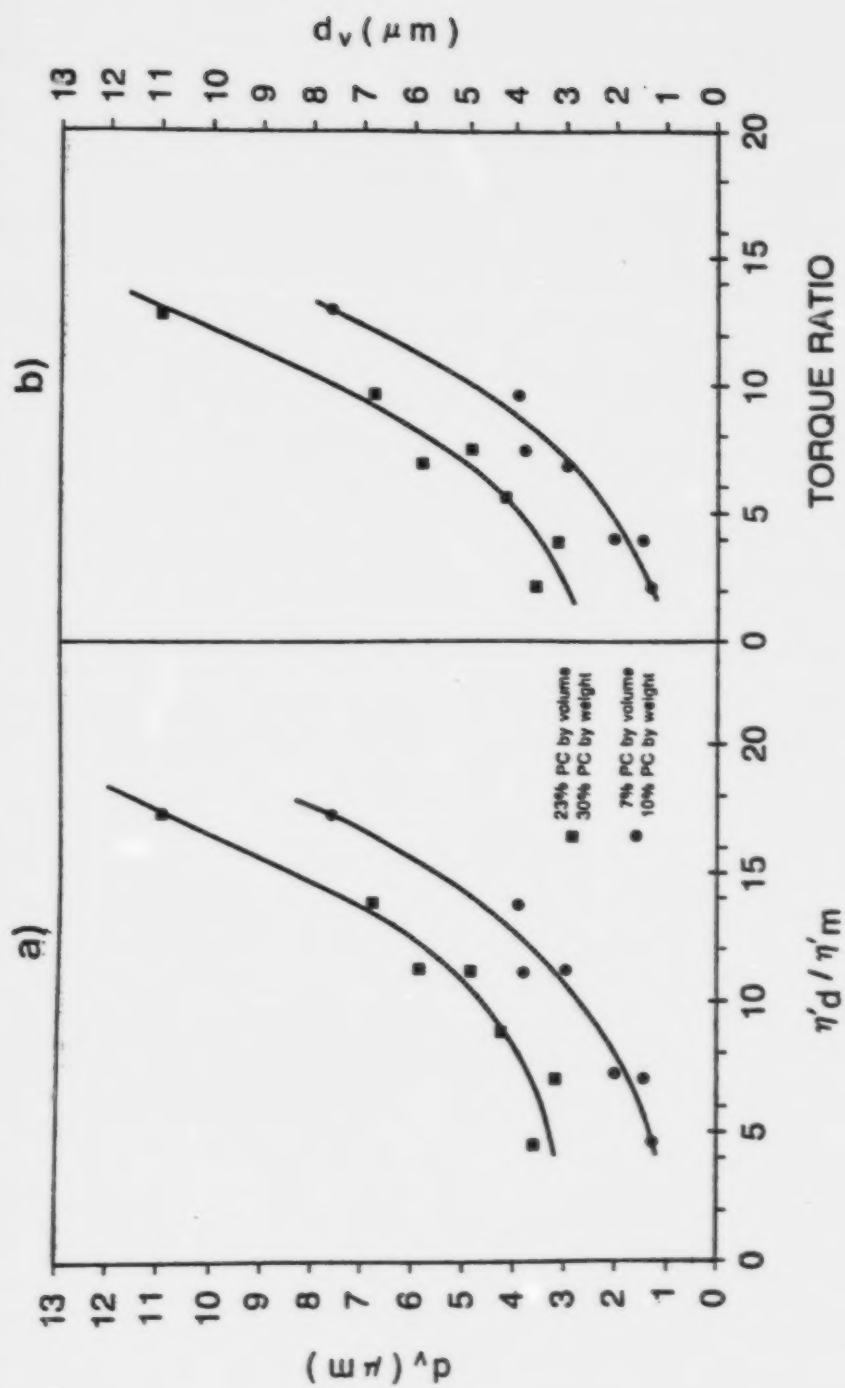


Fig. 5 Volume average diameter versus the a) viscosity ratio and b) torque ratio for P, TR > 1.

and viscosity of the systems are highly interdependent.

Phase size/viscosity ratio dependence for $p > 1$.

In Figure 5 the dependence of the polycarbonate dispersed phase size on both the torque ratio and the viscosity ratio are presented. In the literature the two predominant forms of presenting morphology versus viscosity ratio use the shear viscosity ratio or the torque ratio. The torque in the mixing chamber is a complex combination of shear and elongational flow but is a representation of the flow field in the actual mixing environment. The shear viscosity ratio on the other hand is measured on separate rheological equipment. In our case we have calculated the shear viscosity ratio in the dynamic mode between parallel plates.

An empirical expression, developed by Brabender for the type 6 mixing head used in this study, was used to calculate an average shear rate in the mixing chamber ($\dot{\gamma} = \text{RPM} \times 3.7$) [24,25]. 50 rpm corresponds to a shear rate of 185 s^{-1} . In order to calculate the viscosity ratio, the viscosity at 100 rad/sec (corresponds to 100 s^{-1}) for the virgin materials was used. This value is very close to the empirically calculated shear rate of 185 s^{-1} in the mixing chamber. Extension of the rheological data from 100 s^{-1} to 185 s^{-1} by power law approximation had little impact on the viscosity ratio.

It is useful to see how these two techniques of characterizing polymer blends compare in Figure 5. The torque ratio value tends to be somewhat less than the viscosity ratio but the shape of the curves and the correlation are very similar. Both torque ratio and viscosity ratio have a good correlation

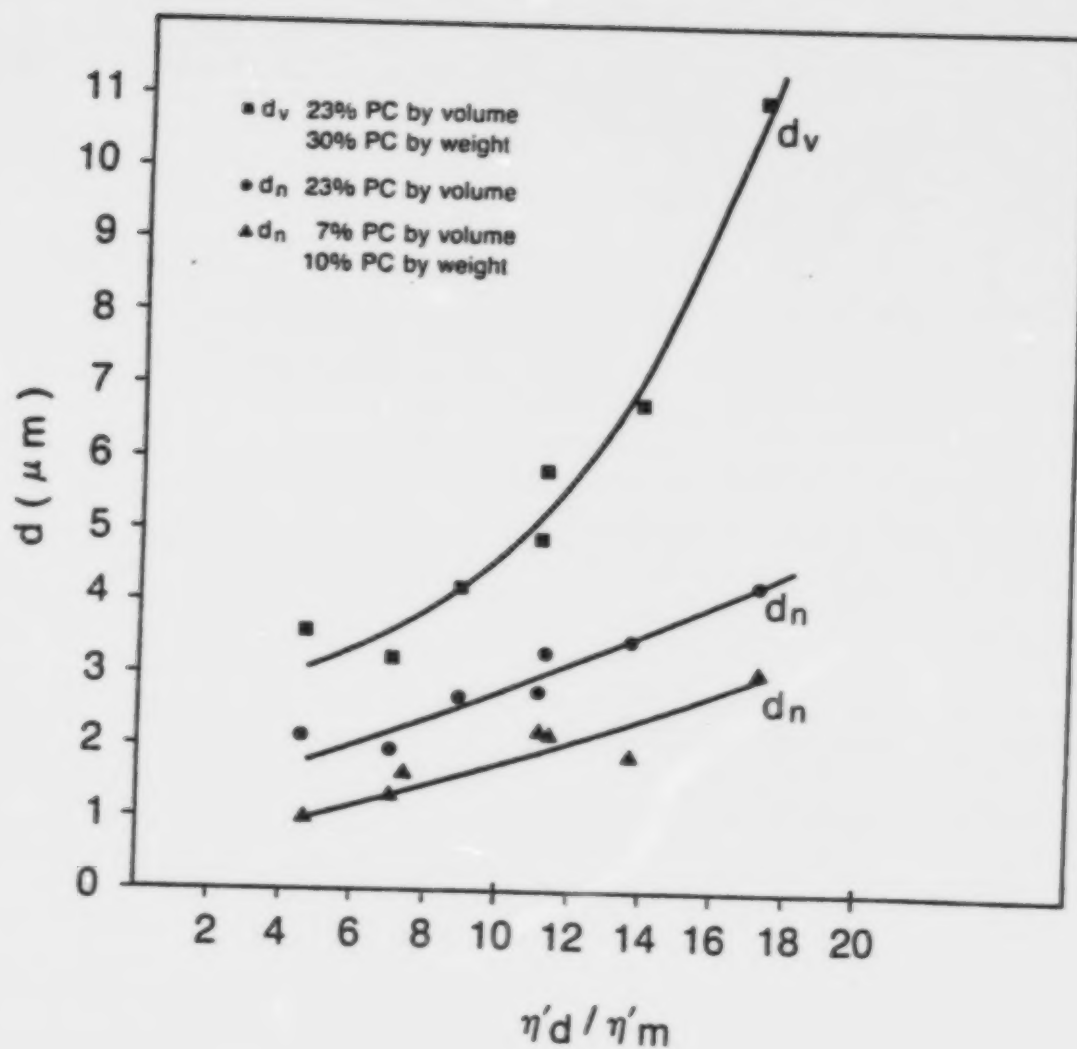


Fig. 6 Comparison of volume average and number average diameter versus viscosity ratio at $p > 1$.

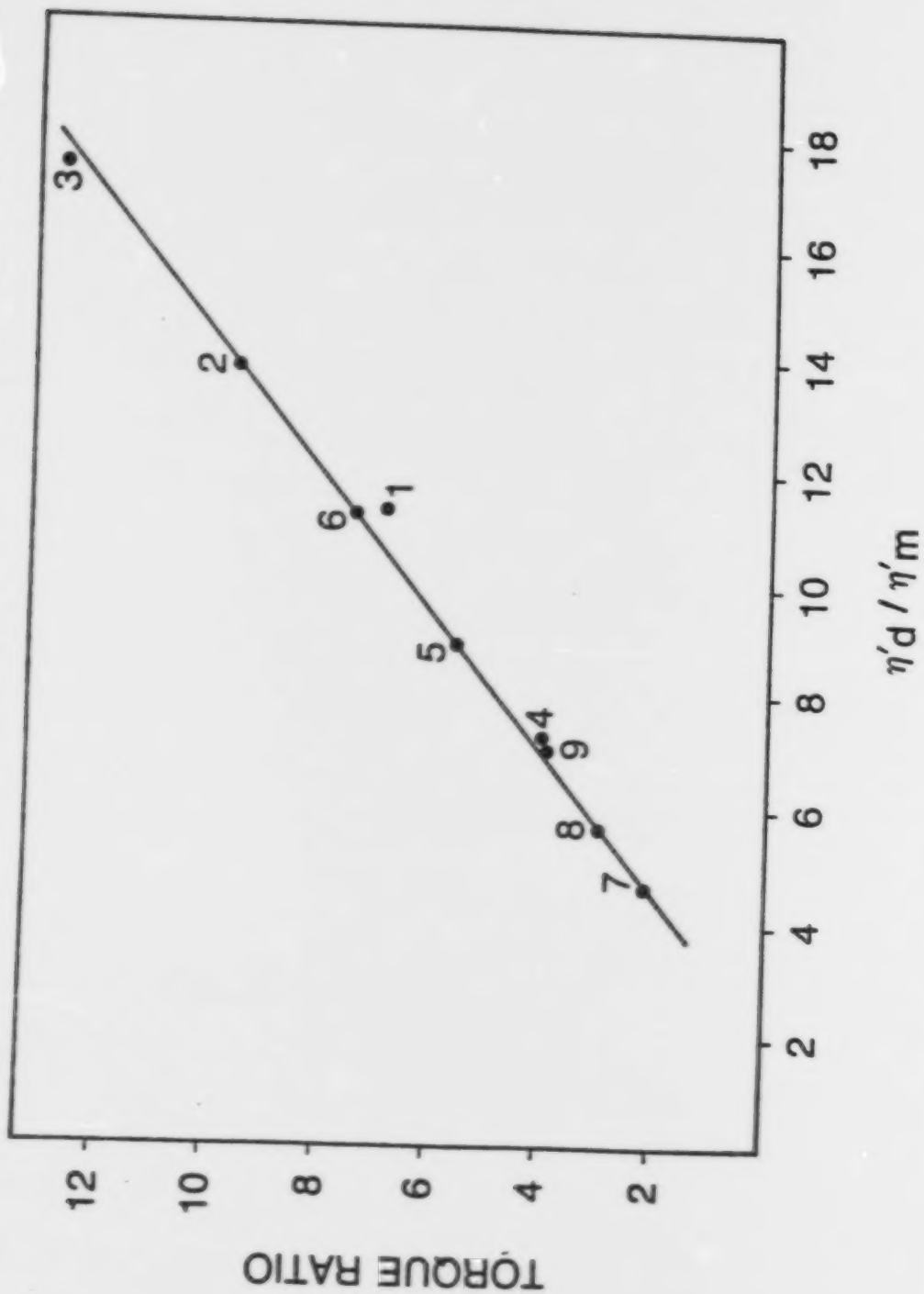
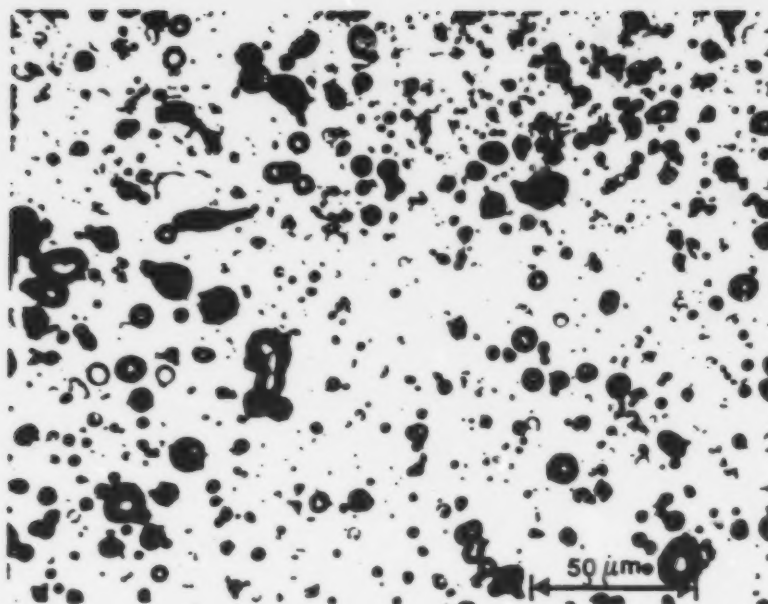
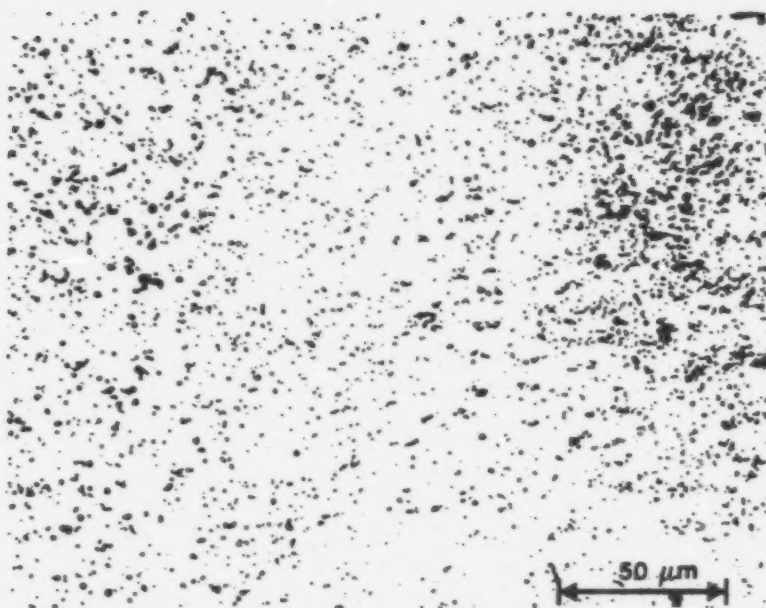


Fig. 7 Correlation of torque ratio and viscosity ratio for all 9 combinations of PC dispersed in PP.



a)



b)

Fig. 8 Light micrograph of 7% PC in PP (volume fraction) at a) $p=17.3$ and b) $p=4.5$.

to phase size. Considering the different methods used, Fig. 5a and 5b correlate well. The differences may be attributed to the fact that the flow field in the mixing chamber is a combination of extensional and shear flow and also that the shear rate calculated in the chamber is an approximate value. The close correlation observed indicates that although some elongational flow is certainly present in the mixing chamber the predominant flow field controlling morphology in the mixing chamber is likely shear flow. This is further emphasized in Fig. 7 where the torque ratio and the shear viscosity ratio are shown to be in direct correlation.

In Figs. 5 and 6 we see the significant effect of viscosity ratio on the size of the minor phase. Light micrographs are shown in Fig. 8. At 30%PC the volume average diameter varies from $1.5\mu\text{m}$ at $p = 4.5$ to $12\mu\text{m}$ at $p = 17.3$. The number average diameter varies from $1\mu\text{m}$ to $3\mu\text{m}$. Several comments can be made concerning Figs. 5 and 6: the volume average diameter has a strong dependence on viscosity ratio, the shape of the curve is not affected by increasing the concentration of the minor phase and the number average diameter has a more linear-like dependence on viscosity ratio.

It is important to note that even at a viscosity ratio of $p = 17.3$ significant particle disruption has occurred unlike Newtonian systems in a shear flow field which do not disrupt above $p = 4$. Both Schreiber [26] and Wu [13] have also reported significant deformation of the minor phase for viscoelastic systems at high viscosity ratios. Compared to Newtonian systems these data follow a more flattened profile although the volume average diameter versus p in Fig. 5 indicates that disruption is becoming much more

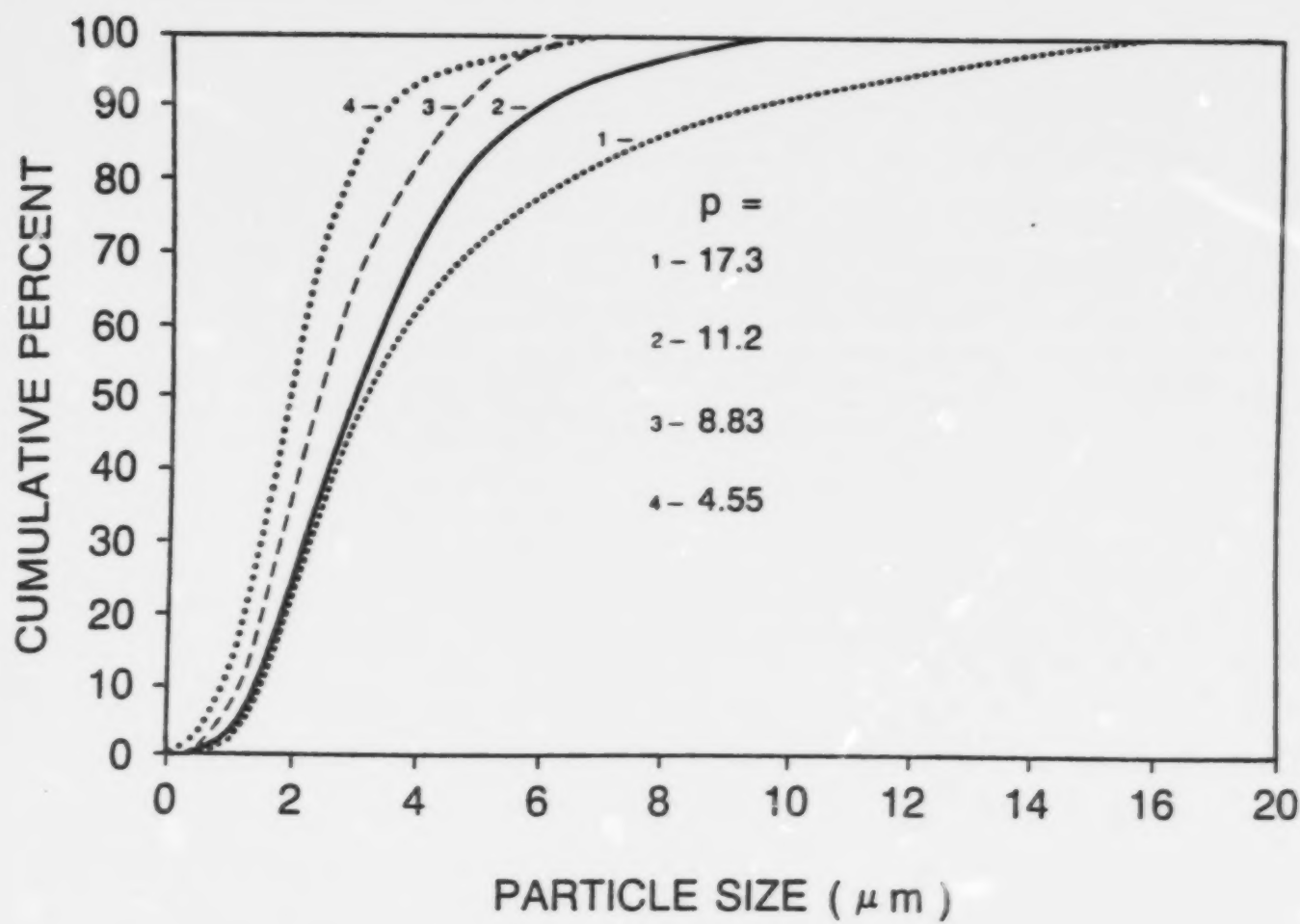


Fig. 9 Size distribution curves for 23% PC in PP (volume fraction) at various viscosity ratios.

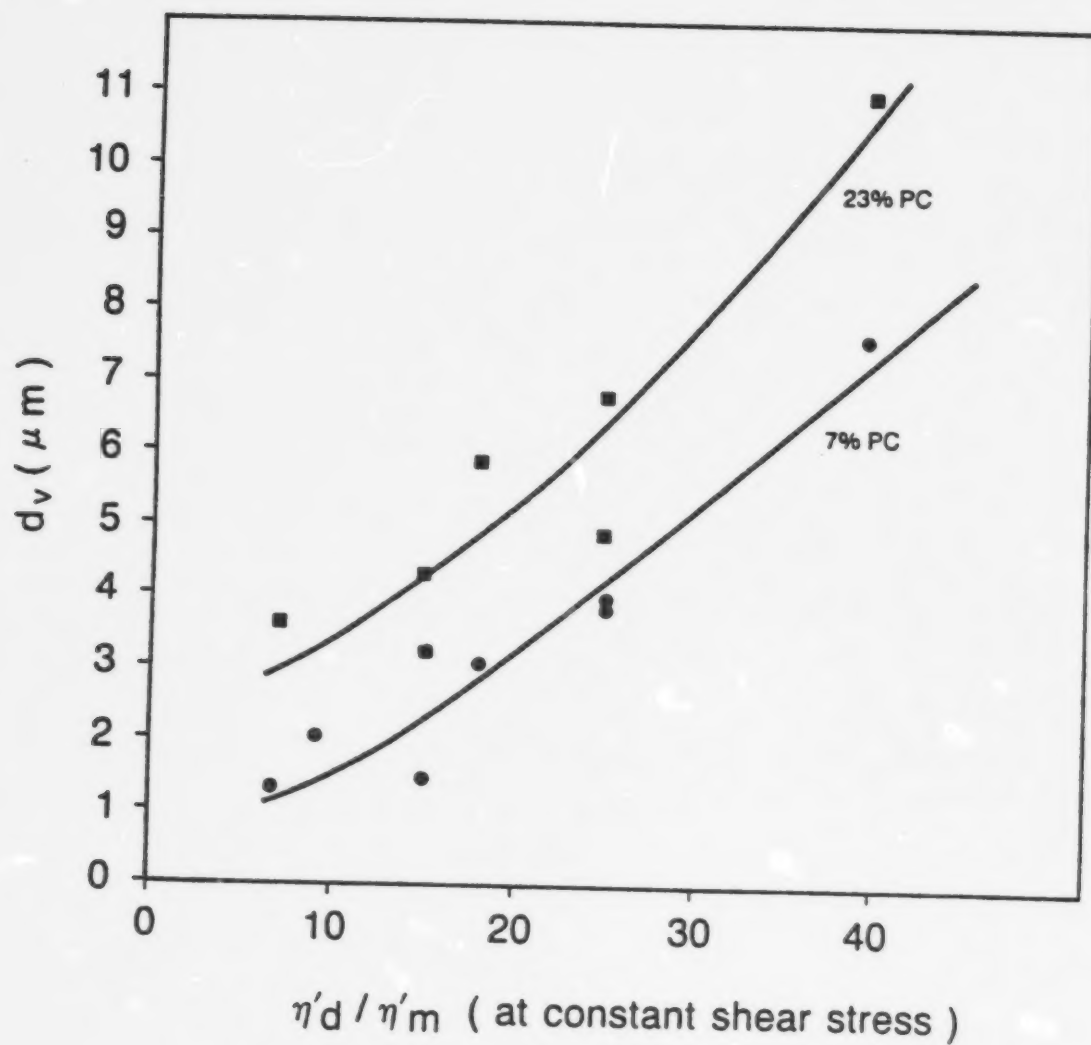


Fig. 10 Volume average diameter versus the viscosity ratio calculated at constant shear stress for $p > 1$.

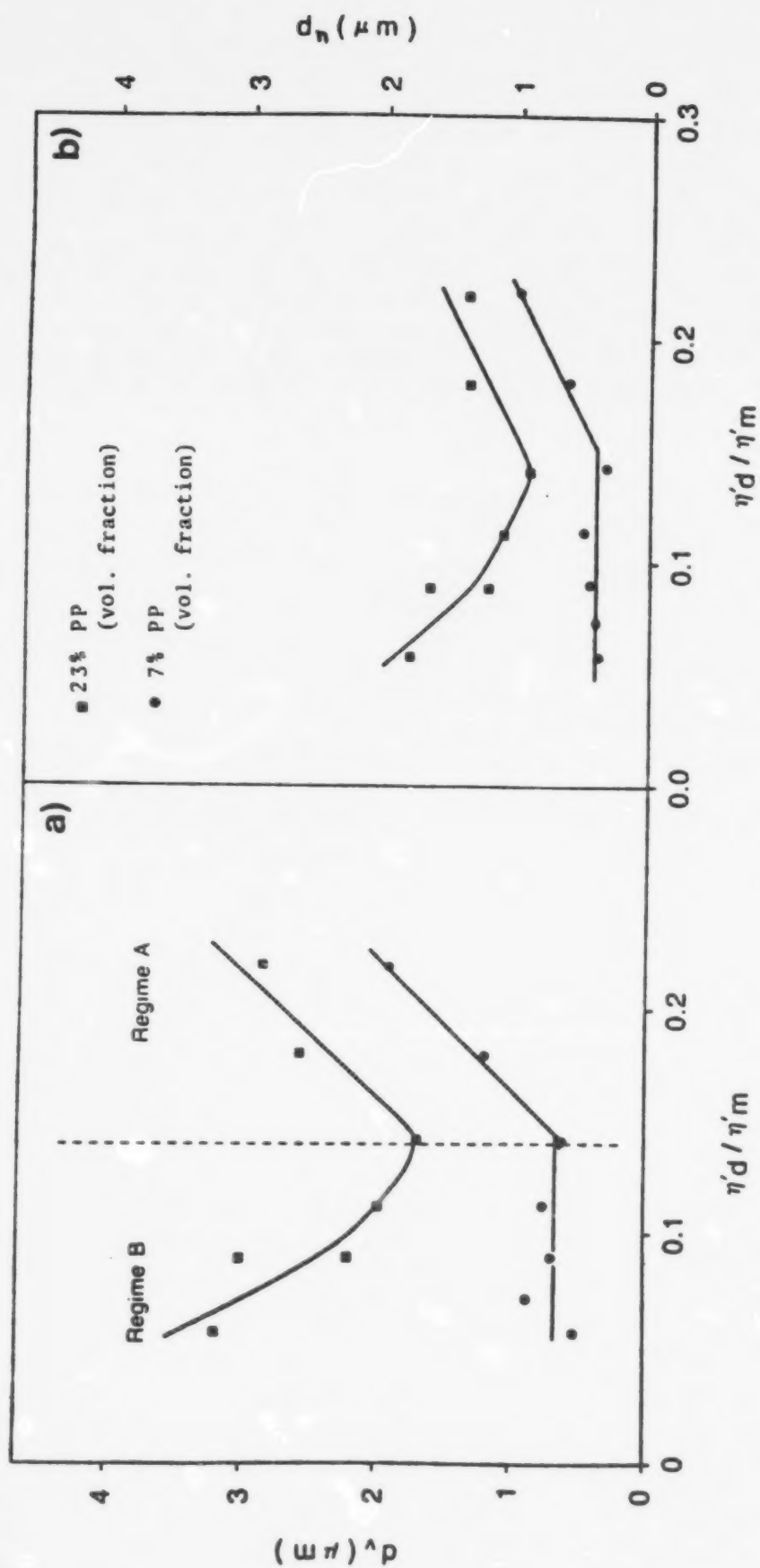
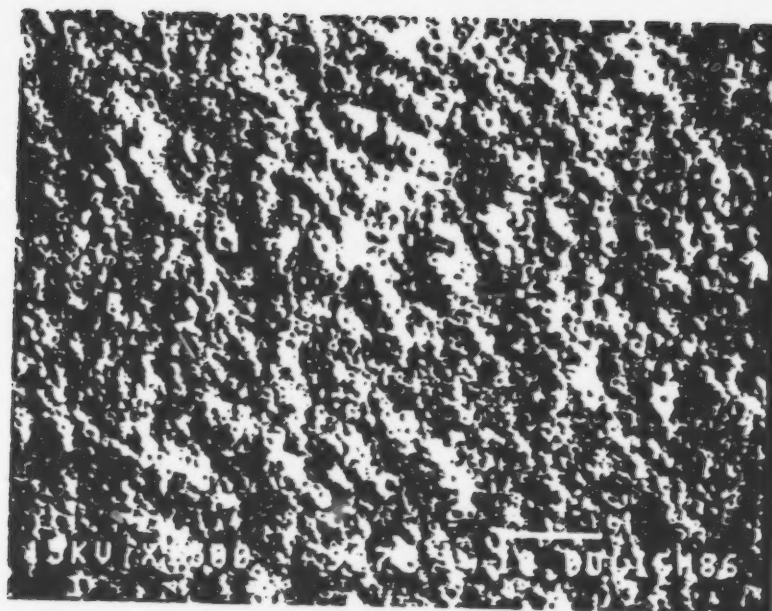


Fig. 11 a, b) Volume and number average diameter versus the viscosity ratio at $p < 1$.

12/27

a)



10 μ m

b)

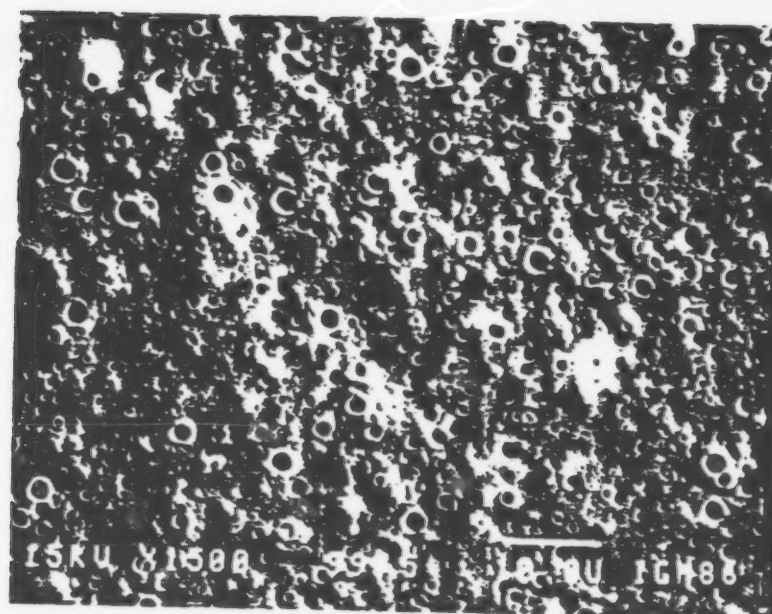
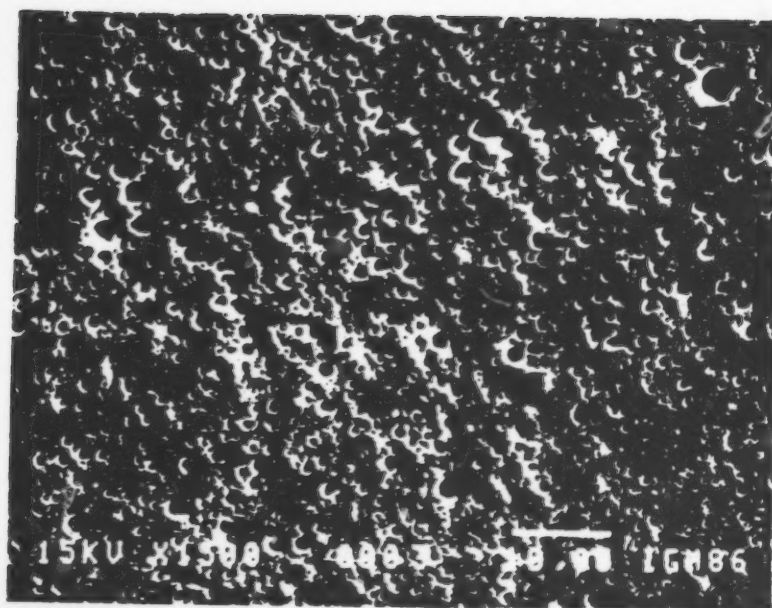
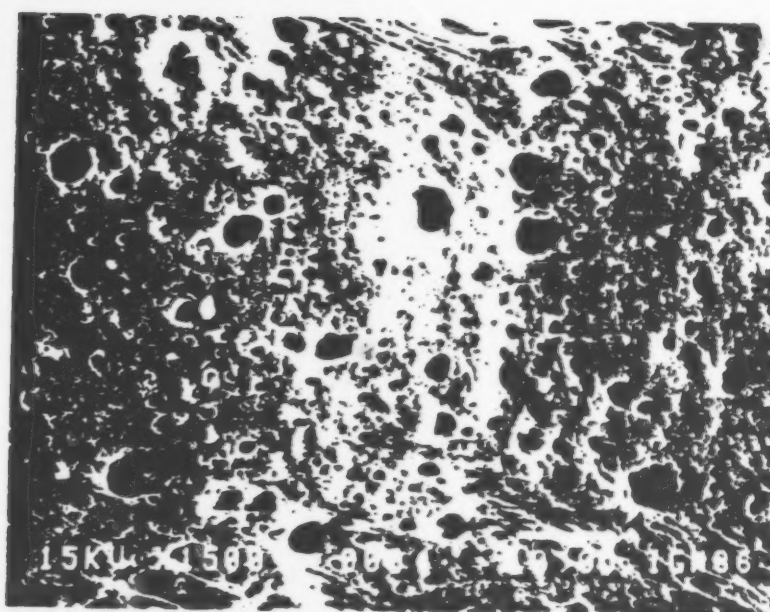


Fig. 12 Scanning electron micrographs for 7% PP dispersed in PC (volume fraction) at a) $p=0.11$ and b) $p=0.22$.



a)


10 μ m

b)

Fig. 13 Scanning electron micrographs for 23% PP dispersed in PC (volume fraction) a) $p=0.14$ and b) $p=0.058$.

difficult at high p for these systems and likely indicates the approach to an upper limiting viscosity ratio for particle deformation. Fig. 9 indicates that the polydispersity in the size of the minor phase increases with increasing viscosity ratio. In all cases observed to date the size distribution becomes more polydisperse as particle size increases.

Han [1] has reported that the shear stress may be more continuous at the interface than shear rate. In Figure 10 the phase size is plotted versus the viscosity ratio calculated at constant shear stress (based on the shear stress for the matrix at 100s^{-1} .) The viscosity ratio calculated at constant shear stress is significantly higher than that calculated at constant shear rate due to the significant differences in viscosities of the two components. It is interesting to note that the trends observed in Fig. 5 hold in Fig. 10, but in the latter the correlation is poorer rather than improved.

Phase size/viscosity ratio dependence at $p < 1$.

In Fig. 11 the phase size versus the viscosity ratio is shown for polypropylene dispersed in polycarbonate (PP/PC) at two concentrations. Both number and volume average diameters are shown. Some corresponding electron micrographs are shown in Figs. 12 and 13. At low concentration it can be seen that a minimum particle size is achieved at $p = 0.15$ ($TR = 0.25$). Above this value particle size increases whereas below this value a plateau is maintained. These results compare well with studies carried out on Newtonian fluids in shear flow fields. In those classical studies the minimum in the critical energy for deformation extended from a viscosity ratio of 0.1 to 1 in

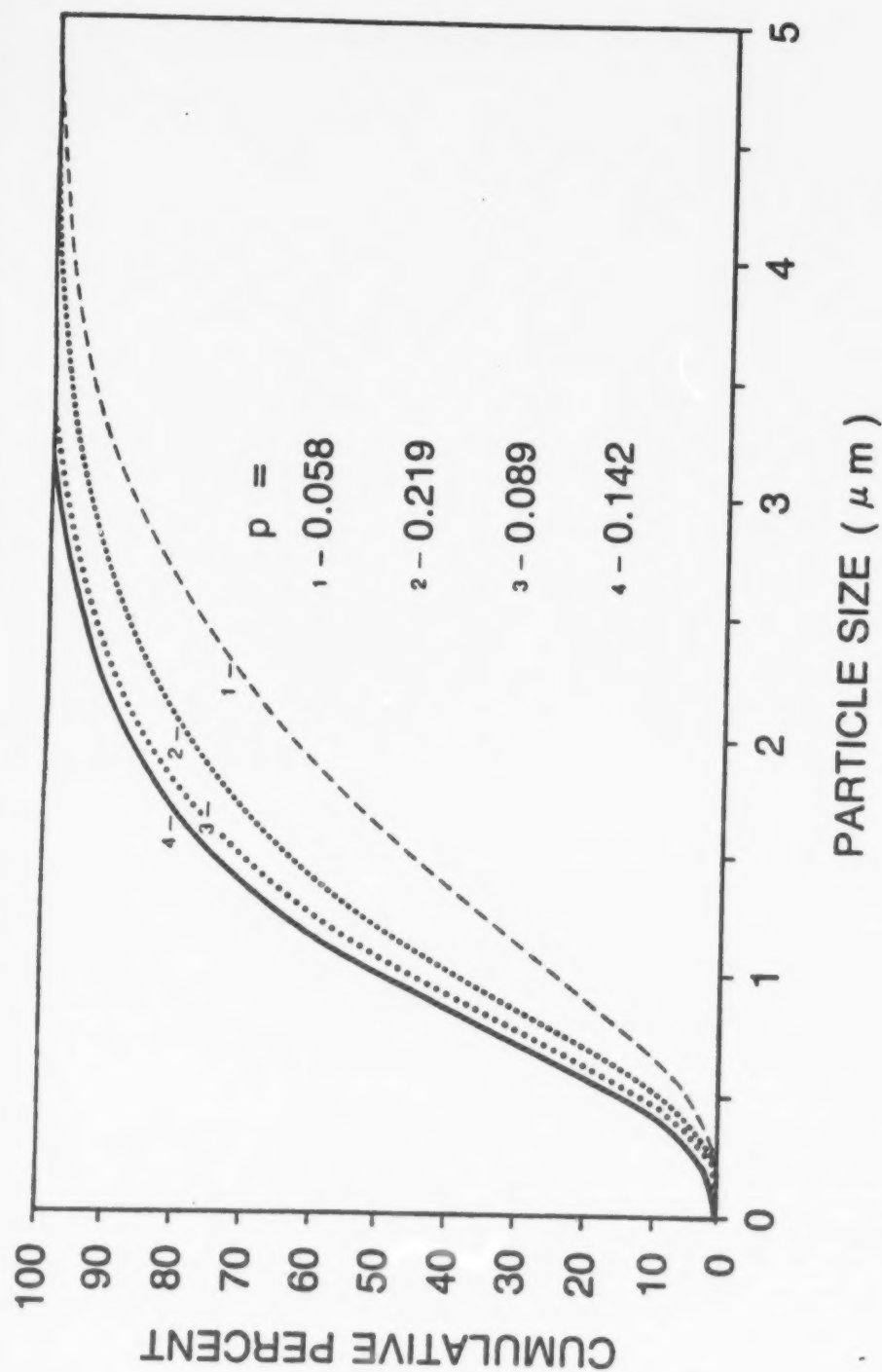


Fig. 14 Size distribution curves for 23% PP in PC (volume fraction) at various viscosity ratios.

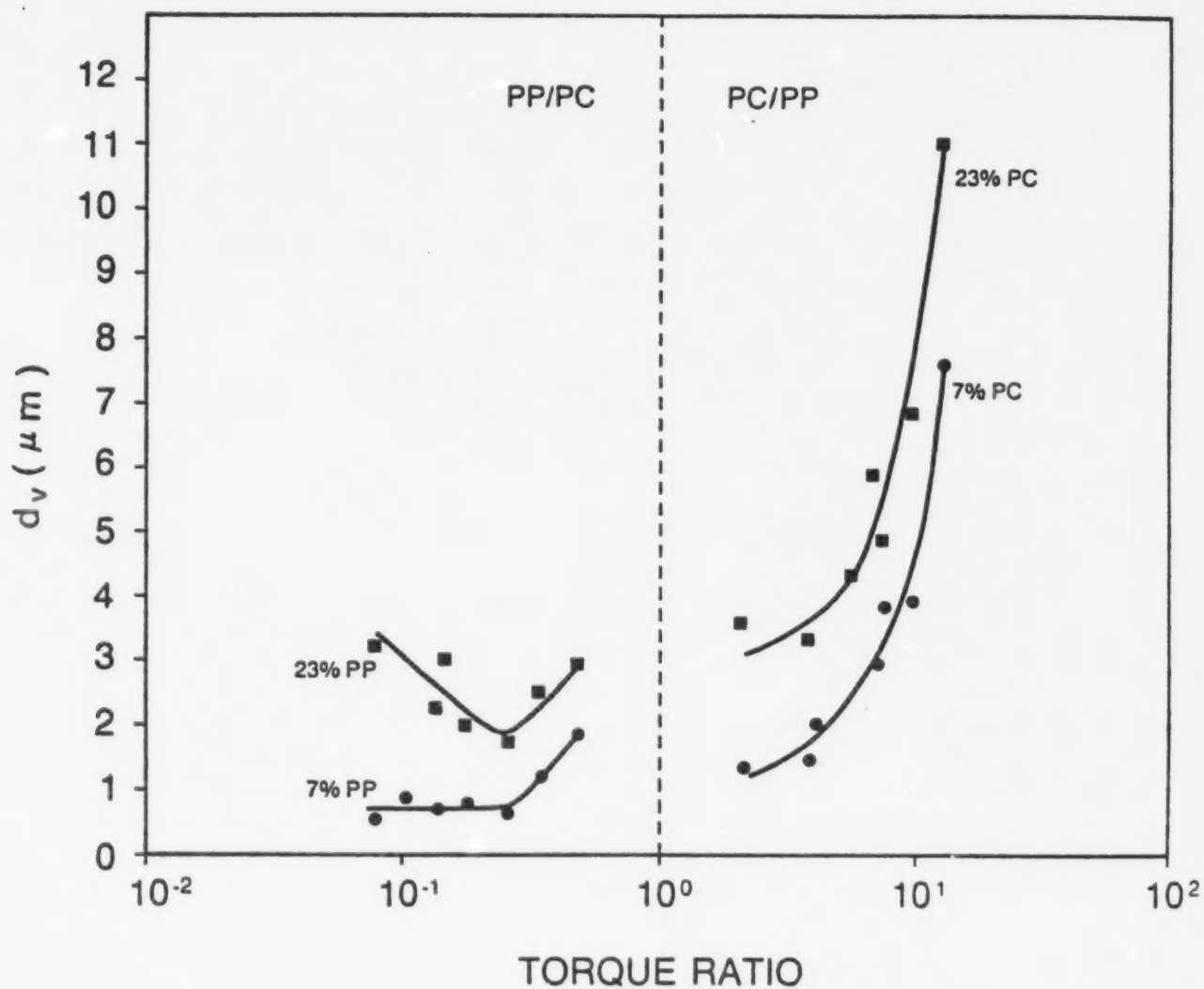


Fig. 15 Volume average diameter versus torque ratio from TR of 0.078 to 12.8.

uniform shearing flow. The true minimum however occurred at a viscosity ratio of ~ 0.2 for Tavgac. Taylor observed the minimum at a p of approximately 0.3. The above classical studies were carried out at low concentration in order to minimize particle-particle interactions. The minimum observed in the present experiments closely corresponds to that observed in the above data, however the minimum is sharper with plateau behavior observed only at low concentration.

At higher concentration the shape of the curve in Regime A (above the minimum) is little affected by the change in concentration. Regime B however shows significant concentration dependence. The results indicate that increasing the concentration has a significant effect on the plateau region, with essentially no minimum plateau existing at high concentration. Rather, a very sharp minimum is observed and the curve has a V-shape appearance with significant increase in particle size observed above and below $p \approx 0.15$. It is interesting to note that the position of the minimum appear to correspond at both low and high concentration. Wu [13] has suggested that the minimum particle size occurred at approximately $p = 1$ with particle size increasing at $p < 1$ for nylon/rubber systems. However, the few number of data points below $p = 1$ in his studies made absolute conclusions difficult. The particle size distribution curves for 23% PP in PC are shown in Fig. 14.

The combined results obtained over the entire viscosity range are shown in Fig. 15. Inversion of the phases appears to have some effect on the morphology as the curves do not seem to be strictly continuous. Examination of the 23% curve in Fig. 15 clearly illustrates lower and upper limits to the

viscosity ratio beyond which deformation of the minor phase becomes more difficult.

From the practical perspective this work indicates that the general consideration of a minimum occurring at $p = 1$ is not universally true. A significant reduction in particle size was achieved below $p=1$ for these systems. In these studies the minimum was observed at a TR of 0.25 (see Figs. 11 and 15) and $p = 0.15$. The results indicate that at low concentration (10% or less) a good region for processing blends (where the matrix is highly viscous) may be in the plateau region. At higher concentration one can expect complex phenomena to occur below the minimum and it may be difficult to process morphologically reproducible structures.

Studies are underway to correlate this data to work carried out on commercial compounding equipment and also to elucidate the effect of an interfacial agent.

CONCLUSIONS

The size of the minor phase has been studied quantitatively as a function of the viscosity ratio, p , at $p > 1$ and $p < 1$.

When $p > 1$ (polycarbonate dispersed in polypropylene) both the number average and volume average diameter of the dispersed phase are highly dependent on viscosity ratio. Significant deformation of the minor phase occurs at p values as high as $p = 17$.

When $p < 1$ (polypropylene dispersed in polycarbonate) a minimum particle size is achieved at $p = 0.15$ (torque ratio ≈ 0.25). Below this value at low concentration the particle size remains constant within the experimental range studied. At higher concentrations it was found that there is a lower limiting viscosity ratio beyond which deformation of the minor phase becomes more difficult. These phenomena can be correlated to the behavior of Newtonian fluids in shear flow.

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Light-scattering characterization of polyblends
in the presence of multiple-scattering conditions

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Abstract:

A novel approach is described for the noncontact evaluation of structural morphology in polyblends by light scattering. Optical methods are attractive for the on-line characterization of translucent materials because they are noninvasive, rapid and applicable to high temperature materials. One limitation of the light-scattering techniques is their applicability to relatively thin samples in order to avoid multiple-scattering effects which smear out the details of the light diffraction pattern. The methods described in this paper circumvent this limitation and may also be applied to very thick parts which are inspected with access to a single side of the material. Results are presented for polypropylene-polycarbonate (PP/PC) samples of different thicknesses and microstructural morphology, including fibrillar-type oriented structures.

INTRODUCTION

The accelerating industrial trend toward factory automation and Computer Integrating Manufacturing (CIM) is creating an urgent need for on-line sensors to continuously monitor the relevant production parameters. Such sensors should be rugged, reliable, compact and easy to apply in hostile environmental conditions or for monitoring high-temperature materials.

Optical sensors are ideal candidates for this kind of applications because they operate without requiring a close contact with the material to be inspected. The recent availability of increasingly reliable and inexpensive optoelectronic devices such as semiconductor lasers and integrated optical detectors is also playing a major role in the rapid advancement of this sector of the sensing technology.

The great majority of polymers are immiscible from the thermodynamic standpoint and most "blends of commerce" are immiscible. Immiscible blends form a multi-phase system with a deformable minor phase and under the appropriate conditions morphological structures such as spheres, ellipsoids, fibres and plates/ribbons can be produced. Under certain conditions co-continuous phases may also be formed. The morphological structures mentioned above are generated in-situ while processing and these systems offer the potential to modify the dispersed phase through a wide range of size and shape. Control of these parameters however can be a very complex task. As the commercial importance of these materials becomes more pronounced, it will be necessary to gain a more rigorous

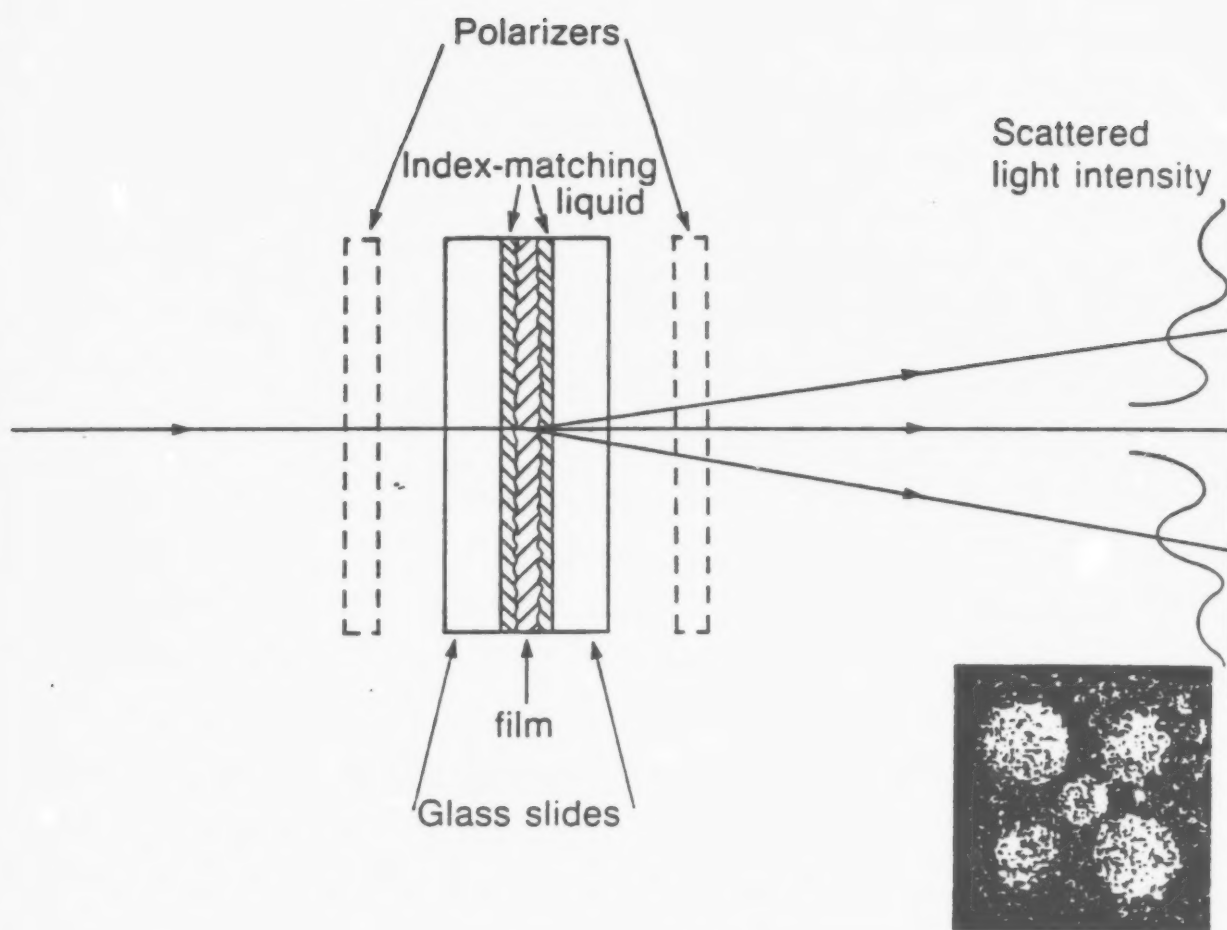


Fig. 1: Schematic diagram of the typical experimental configuration required for polymeric film characterization by angular light scattering.

understanding of how to control the morphology during processing. As a result, the development of rapid on- and off-line characterization techniques to measure the size and shape of the minor phase is important.

A number of optical techniques using angular scattering, spectral turbidimetry and single-side, spot-illumination imaging methods are described in this paper as applied to the analysis of particle size, shape and orientation to PP/PC polyblends. Their applicability to on-line instrumentation needs is discussed.

ANGULAR LIGHT-SCATTERING ANALYSIS OF THIN POLYMERIC FILMS

Optical methods such as birefringent microscopy, infrared dichroism and angular scattering are widely used for the laboratory analysis of polymeric samples (1-3). Light scattering is an attractive approach for the analysis of particulate inclusions whose size is of the order or slightly larger than the light wavelength (1, 4-8). A typical apparatus for the analysis of a polymeric film by observation of its angular light-scattering pattern is shown in Fig. 1. The light beam, usually a visible laser beam, is partially scattered by interaction with the particles contained within the film. The Mie diffraction pattern (9,10) which is produced from the interaction of light with opaque or transparent particles having a refractive index different from that of the matrix is observed on a screen. The features of the scattering pattern are related to the average size and shape of the particles contained within the laser-irradiated volume of the polymeric film. Light polarizing compo-

nents are often added to the basic apparatus in order to analyze optical-activity effects, particularly when anisotropic microstructural features are present within the material.

The angular-scattering approach is only useful in the single-scattering regime. In the case of multiple scattering, i.e. when most light photons are sequentially scattered by two or more particles through the film, the features of the scattering pattern are spread out and eventually lead to a Lambertian, cosine-distributed pattern (11-13). Multiple scattering becomes significant at extinction values (i.e. attenuation of the undeviated beam) of the order of 25% (see, e.g., ref. 14, p. 119).

In order to avoid multiple scattering when analyzing a polyblend film, one must resort either to extreme second-phase dilutions or to very thin samples. In both cases, small-angle light scattering due to surface roughness is normally a major source of perturbation of the angular pattern. Such a problem is normally circumvented by placing the polymeric sample between glass slides and using a matching-index liquid (an oil having a refractive index equal to that of the polymer matrix) to avoid reflections at the liquid-sample interfaces, as Fig. 1 shows. Such an approach is obviously impractical for on-line industrial applications.

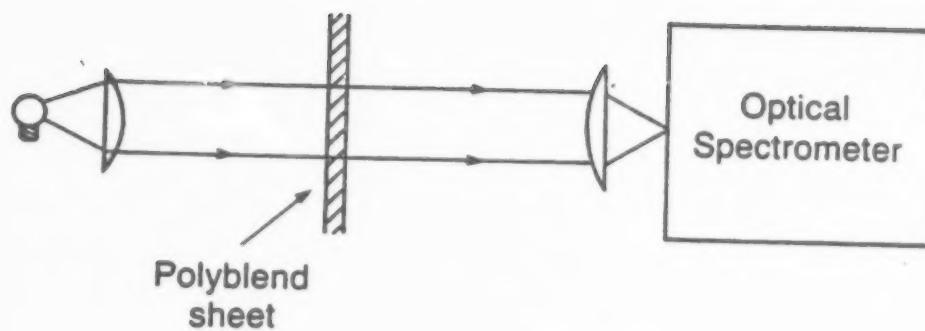


Fig. 2: Schematic optical apparatus used for particle analysis in a polyblend sheet by spectral turbidimetry.

THE SPECTRAL TURBIDIMETRY METHOD

The basic principle of spectral turbidimetry is illustrated in Fig. 2. A wide-spectral-bandwidth light beam is transmitted through the material to be inspected. Part of the light beam will be scattered or absorbed within the material, while the undeviated light is collected by a lens on the entrance slit of a spectrometer situated in the focal plane of the lens. The dispersive components of the spectrometer may equivalently be situated between the light source and the material. The transmitted beam normally suffers a spectrally-selective attenuation, the amount of light scattering being dependent on the ratio between the scatterer size and the light wavelength. The average particle diameter may thus be evaluated from an analysis of the transmittance spectrum. Applications of this technique have been reported for the inspection of aerosols (15, 16), chemical analysis (see ref. 17, p. 156R) and for latex particle monitoring (18-23).

Although quantitative analyses have until now been reported only for single-scattering media, it has been experimentally observed (see ref. 23 as well as ref. 24 pp. 199-207) that the dependence of the spectral transmissivity on the particle diameter is substantially similar in the case of multiple-scattering media. This can be understood in simple terms by the following argument. If the wavelength is smaller than the particle diameter, part of the incident light beam will be reflected or refracted at each particle/matrix interface. The transmitted light beam intensity will thus become negligibly small after a penetration depth whose length

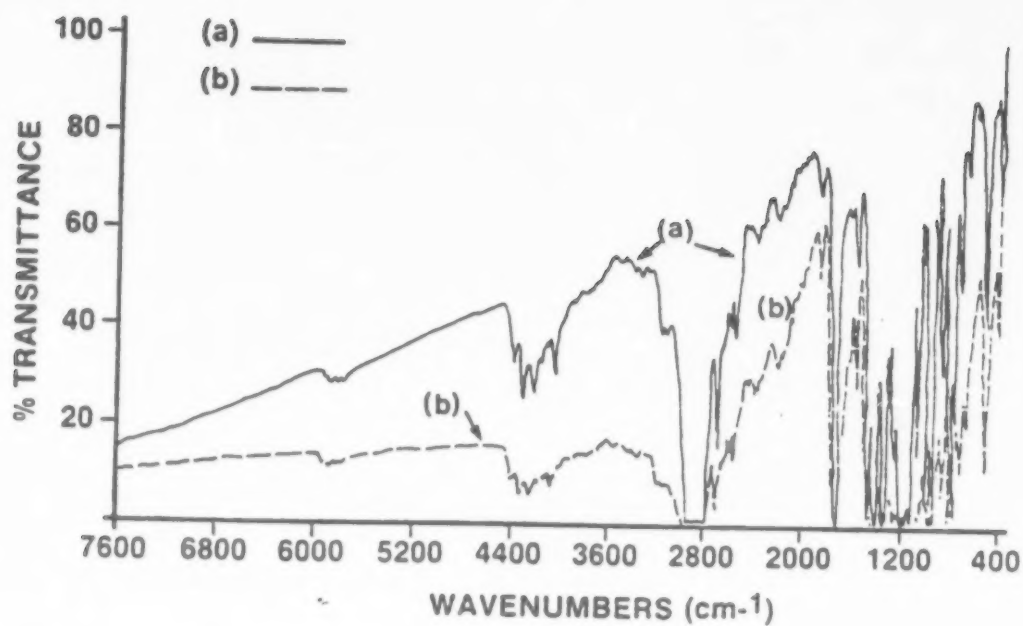


Fig. 3: Infrared transmission spectra obtained with 93% polypropylene - 7% polycarbonate by volume polyblend sheets with average particle diameter (a) 1.6 μm and (b) 18.9 μm .

is determined by the Kubelka-Munk expressions (see, e.g., ref. 25, pp. 420-438). Conversely, wavelengths much longer than the particle diameter are transmitted through the composite medium with negligible attenuation (it may be considered that even perfectly transparent, homogeneous materials are discontinuous at the molecular scale). The average particle diameter may thus be evaluated from the position of the attenuation edge in the spectrum of the transmitted light.

An example of such a spectrum is shown in Fig. 3. The spectral distribution of the transmitted light beam has been recorded with an instrument of the kind shown in Fig. 2 through a 90% polypropylene/10% polycarbonate sample by weight (93% PP/7% PC by volume), nearly 0.2 mm-thick, containing dispersed and nearly spherical PC particles of average diameter (a) in the 1-2 μm range and (b) in the 10-20 μm range. The angular aperture of the spectrometer was of the order of ± 5 degrees. As it can be seen, except for the distinguishable absorption peaks, the transmittance is relatively high in the 2000 to 400 cm^{-1} spectral range for both samples. The transmissivity drops, however, very abruptly near 2000 cm^{-1} (corresponding to a wavelength of 5 μm) for sample (b), while a strong attenuation is only visible starting from the 4000-7000 cm^{-1} range for sample (a) containing an equal volume of smaller PC particles.

Average particle-size analyses may thus be performed on relatively thick polyblend films containing components with different refractive indices and particle sizes in the 1 to 20 μm range. Such analyses are

important because the particle size and distribution of the minor phase of a polymer blend can have a significant effect on both the melt rheology and the mechanical properties (especially impact strength) of the system. The particle range may be extended to the 0.1 to 1 μm area by resorting to near-IR/VIS/UV spectrometric devices. An inexpensive process analyzer based on this approach could be realized using a number of optical filters to probe the transmitted light intensity at a few selective spectral regions. The average particle diameter could be estimated from such readings using a calibration curve.

Furthermore, it can be seen from observation of curve (b) in Fig. 3, in the range from 3000 to 7600 cm^{-1} , that the attenuation introduced by a polyblend film of given thickness and particle contents is practically independent of the chosen spectral area when the wavelength is larger than the particle diameter. By probing the transmissivity through the film at sufficiently short, and absorption-free, wavelengths, the absolute level as well as the fluctuations of the particle concentration value can be evaluated if the film thickness and average particle size are known. Turbidimetric or nephelometric instruments based on similar principles have been used in industry (see, e.g., ref. 26, p. 6.95), mainly for monitoring the turbidity of liquids such as wastewaters or pulp and paper slurries.

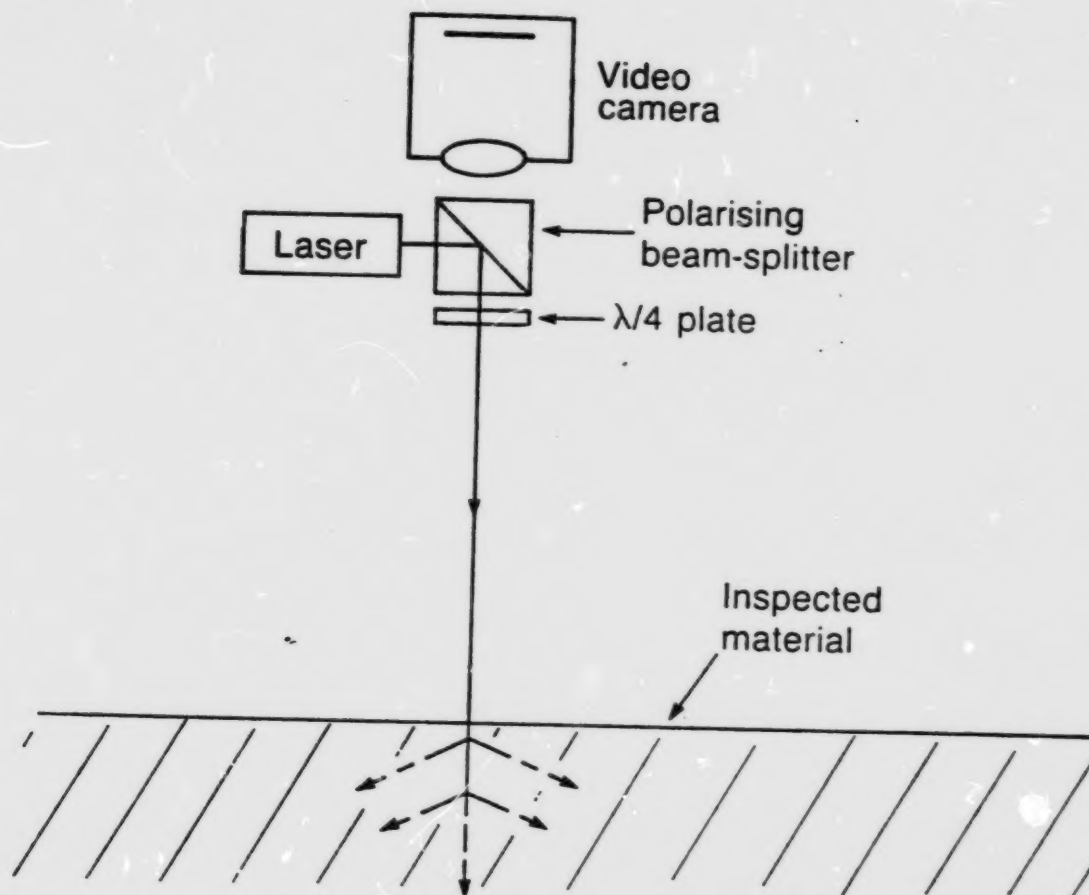
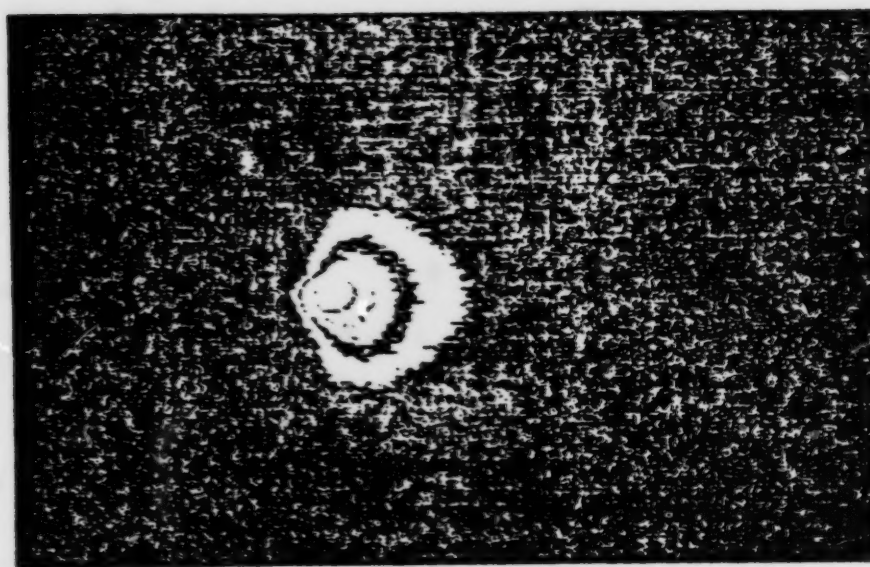


Fig. 4: Single-side imaging approach for the evaluation of particle concentration in thick polyblend sheets.



a

1mm
┌───┐

b

Fig. 5: Examples of images obtained with a single-side imaging method when inspecting a PP/PC polyblend sample with PC volume concentrations of (a) 5% and (b) 16%.

SINGLE-SIDE IMAGING FOR CONCENTRATION ANALYSIS

In many occasions the polyblend sheet is too thick, or its thickness is not continuously known during the manufacturing process, for an effective concentration analysis by the light-transmission approach. One-side configurations of the kind which has been previously used for the evaluation of porosity contents in sintered zirconia ceramics (27) may be used in such circumstances. A typical apparatus is shown in Fig. 4. A narrow laser beam is projected on the surface of the thick sample, and the illuminated spot is observed with a video camera. A polarizing beam-splitter followed by a properly oriented $\lambda/4$ plate may be used to avoid glossy reflections from the front surface of the polymeric sample (alternatively the laser beam may be incident at an angle to avoid the specular reflection). The laser beam penetrates within the material to a depth which is determined by the number of scattering particles along its path. The illuminated area seen by the camera will appear as a narrow and highly luminous spot for materials having a dense particle concentration, while covering a wider surface with a lower peak intensity in the case of lower particle concentrations.

An example of the recorded pictures is given in Fig. 5 (the colors in the original pictures correspond to iso-intensity levels, in equal increments from darkness to saturation of the CCD sensing elements). They were obtained by illuminating optically thick PP/PC plates with a He-Ne laser beam (of wavelength 633 nm) using a configuration of the kind shown

in Fig. 4. The laser beam, of diameter smaller than 1 mm, was in this case incident at 45° with respect to the normal to the sample which contained particles elongated in a direction parallel to the plane of incidence; this is responsible for the peculiar shape of the iso-intensity curves, as will be discussed later. Pictures (a) and (b) in Fig. 5 correspond to samples containing 5 and 16%, respectively (by volume), of PC in PP. The laser intensity was adjusted in order to obtain the same peak intensity in the highest intensity spot for the two cases. Under these circumstances, the iso-intensity curves of the image corresponding to the higher particle concentration extend over a much smaller area as compared to the respective curves obtained with the lower-concentration sample. This is in agreement with the above considerations stating that a higher particle concentration leads to a larger intensity gradient around the illuminated spot. By integrating the total light intensity over images (a) and (b) in Fig. 5 one obtains a parameter which is strongly related to the particle contents, as Table 1 shows.

Table 1: Results of turbidimetric analyses on two polyblend samples

Type of Material	Integrated intensity, single-side imaging approach (percent of full intensity image)	Intensity transmitted through a 3 mm-thick sample (percent of incident intensity)
95% PP/5% PC (vol) 93% PP/7% PC (wt.)	10	15
84% PP/16% PC (vol) 78% PP/22% PC (wt.)	2.5	2

It can be seen that such a parameter is almost as sensitive to particle concentration as the through-transmissivity which was measured for comparison through 3 mm-thick samples of similar materials.

The single-side imaging method is a convenient method (single side, applicable to thick parts, noninvasive and requiring no sample preparation) for evaluating particle concentration if the particle size and the refractive index differential between particle and matrix are known. Inversely, the average particle size may be estimated with the same technique if the particle concentration is known. This can be understood if we consider that the scattering coefficient for particle sizes larger than the light wavelength is linearly related to the total surface of the particles encountered along the light beam path.

The scattering coefficient is thus proportional to Nd^2 where N is the number of particles per unit volume and d the particle diameter. On the other hand, the particle density N is proportional to d^{-3} for a given volume concentration. This results in a scattering coefficient inversely proportional to the particle diameter. The average particle diameter will thus be proportional to the apparent diameter of the illuminated area in an image of the kind shown in Fig. 5. Finally, it should be mentioned that spectral turbidity methods of the kind described in the last section could be combined with the single-side imaging approach by varying the wavelength of the projected laser beam. Single-side particle-size monitoring would be possible by such an approach.

ORIENTATION ANALYSIS OF POLYBLENDS BY LIGHT-SCATTERING IMAGING

The shape of the minor phase is of critical importance. Deformation of the minor phase in the direction of extrusion can significantly improve the % elongation in the machine direction (28), even in the absence of chemical compatibilization. Another novel example of the importance of morphology in immiscible blends is illustrated in the Selar^R technology (nylon/HDPE/ionomer), where the minor phase in the form of platelets can result in significant improvement in barrier properties with respect to hydrocarbons. The possibility to analyze by light scattering the particle shape and orientation in polyblends is considered in this section.

Analysis of polyblend ribbons

Thin sheets of oriented 90% polypropylene-10% polycarbonate by weight (93% PP/7% PC by volume) films were extruded through a slit die on a Brabender Plasticorder Model EPL-V5501. A three-quarter inch single-stage screw was used with an L/D of 25 and a compression ratio of 3:1. The films were extruded at 250°C with a descending temperature profile of 250, 245, 240, 235°C from die to hopper. As the film exited from the die, it was immediately placed in contact with chilled polishing rolls. The rotation speed of the rolls, V_R , was varied from a speed equivalent to the extrusion output, V_E , (no stretching, hot stretch ratio = 1) to an HSR of 10.4. The hot stretch ratio (HSR) is defined

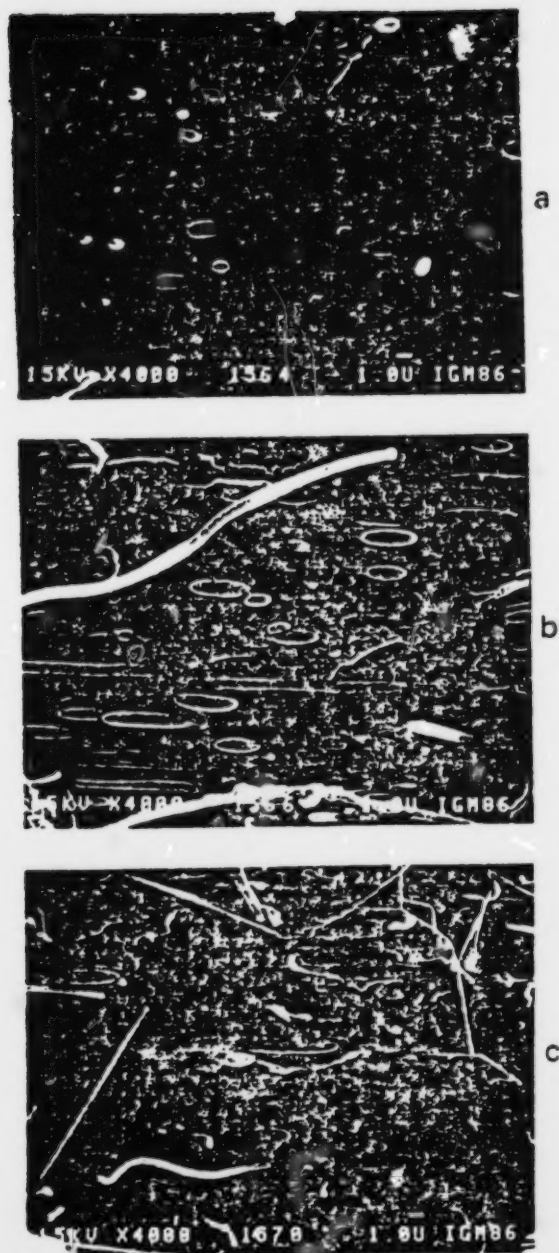


Fig. 6: Electron micrographs obtained in the center of a longitudinal section of 93% PP/7% PC (by volume) extruded ribbons with HSR values of (a) 1, (b) 5, and (c) 10.4.

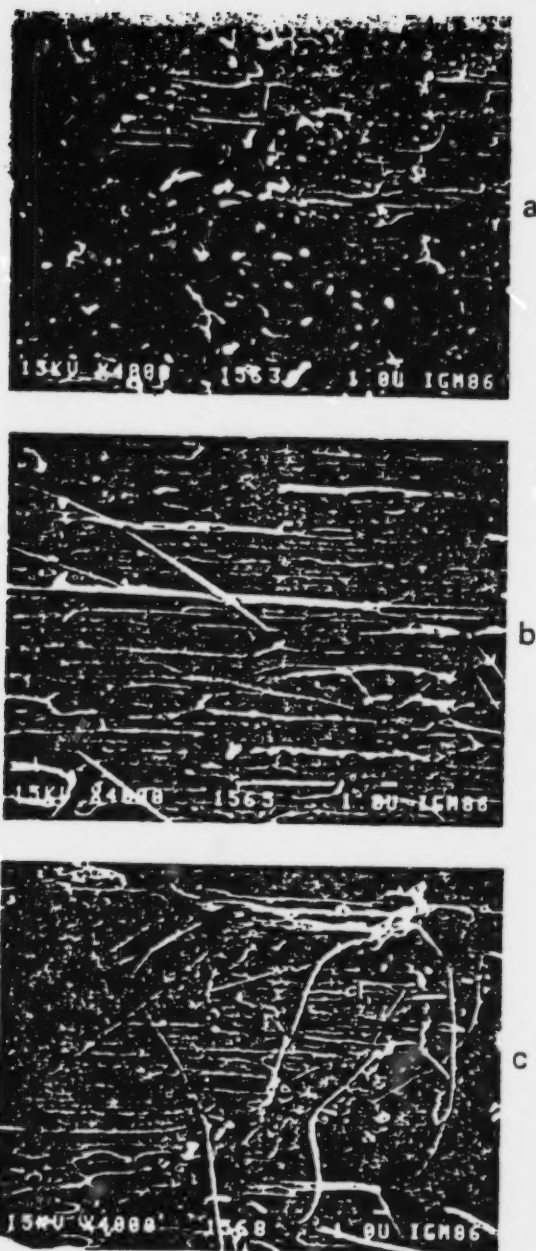


Fig. 7: Electron micrographs of the same samples as in Fig. 6, but taken near the edge of the ribbons, for HSR values of (a) 1, (b) 5 and (c) 10.4.

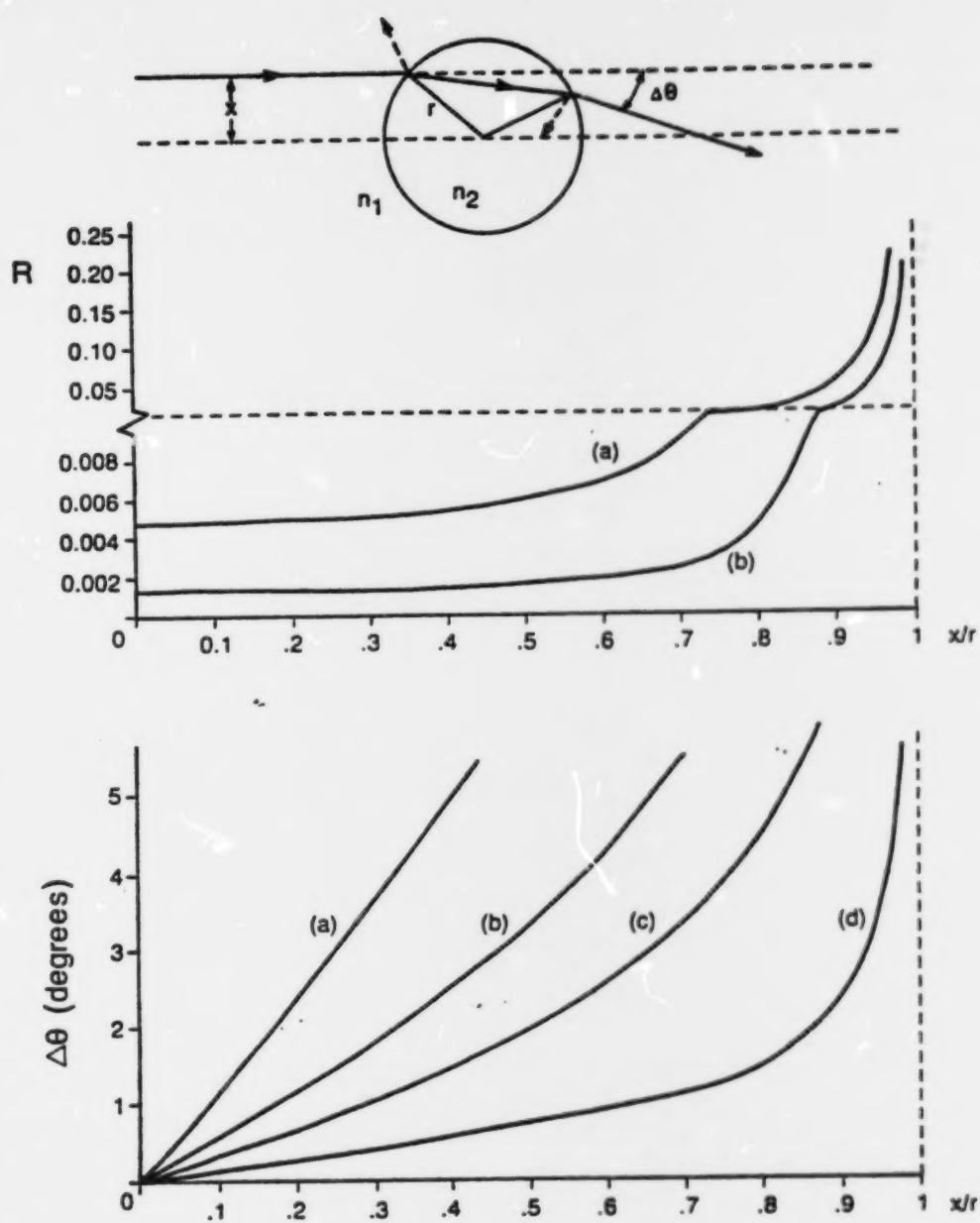


Fig. 8: Schematic ray diagram (top), double-surface reflectivity (middle) and angular deviation (bottom) for the interaction of a light beam with a fiber-like inclusion of diameter much larger than a light wavelength. The computations refer to a ratio n_1/n_2 of the refractive indices of the matrix and fiber materials equal to (a) 0.90, (b) 0.95, (c) 0.97, and (d) 0.99.

as $(V_R - V_E)/V_E$. Using different drawing speeds, three sheets were obtained with an HSR of 1, 5 and 10.4 respectively for the three ribbons of 200, 100 and 70 μm in thickness. Electron micrographs (longitudinal sections) of ribbons extruded at the three hot stretch ratios are shown in Figures 6 and 7. In the absence of stretching (HSR 1), there is a combination of spheres, ellipsoids, and fibers near the edge of the film. In the center of the film very little deformation was observed, spheres were present almost exclusively. At HSR 5 the polycarbonate is highly extended at the edge with some deformation, predominantly an ellipsoidal morphology, in the center. When highly stretched at an HSR of 10.4, the minor phase was in a highly extended fibrous form at the edge and shows a significant level of fiber-like morphology in the center of the film.

The basic principles of the interaction of a nearly parallel light beam with a fiber-like inclusion of diameter much larger than the light wavelength are given in Fig. 8. The fiber acts as a lens whose optical power decreases as the ratio n_1/n_2 between the refractive indices of the fiber and of the matrix materials approaches unity. The attenuation of the light beam travelling in a medium containing a number of fiber inclusions is due to reflection losses and to refractive angular scattering. The reflectivity R suffered by an unpolarized light beam at the fiber-matrix interface can be obtained from the Fresnel expressions (29):

$$R = \frac{1}{2} \left[\frac{\tan^2 (\theta_1 - \theta_t)}{\tan^2 (\theta_1 + \theta_t)} + \frac{\sin^2 (\theta_1 - \theta_t)}{\sin^2 (\theta_1 + \theta_t)} \right] \quad (1)$$

with:

$$\theta_i = \sin^{-1}(x/r) \quad (1a)$$

and:

$$\theta_t = \sin^{-1}(n_1 x / n_2 r) \quad (1b)$$

where x is the distance between the incident light ray and the fiber axis, r is the fiber radius, and n_1 and n_2 are the refractive indices of the matrix and of the fiber materials, respectively.

The middle graph in Fig. 8 shows the double-reflection loss suffered by the light beam as a function of the ray position x/r and for the values of n_1/n_2 of (a) 0.90 and (b) 0.95. The total attenuation suffered by the light beam incident on the fiber cross-section corresponds to the area subtended by the corresponding curve. Even in the case of a large refractive index differential corresponding to $n_1/n_2 = 0.90$ (curve a) such losses amount to a relatively small 2.7%, as it was computed by numerical integration.

The scattering component of the attenuation is normally more important, as can be inferred from the expression of the deviation $\Delta\theta$ undergone by the incident light beam obtained by eqs. (1a) and (1b) above:

$$\Delta\theta = 2[\sin^{-1}(x/r) - \sin^{-1}(n_1 x / n_2 r)] \quad (2)$$

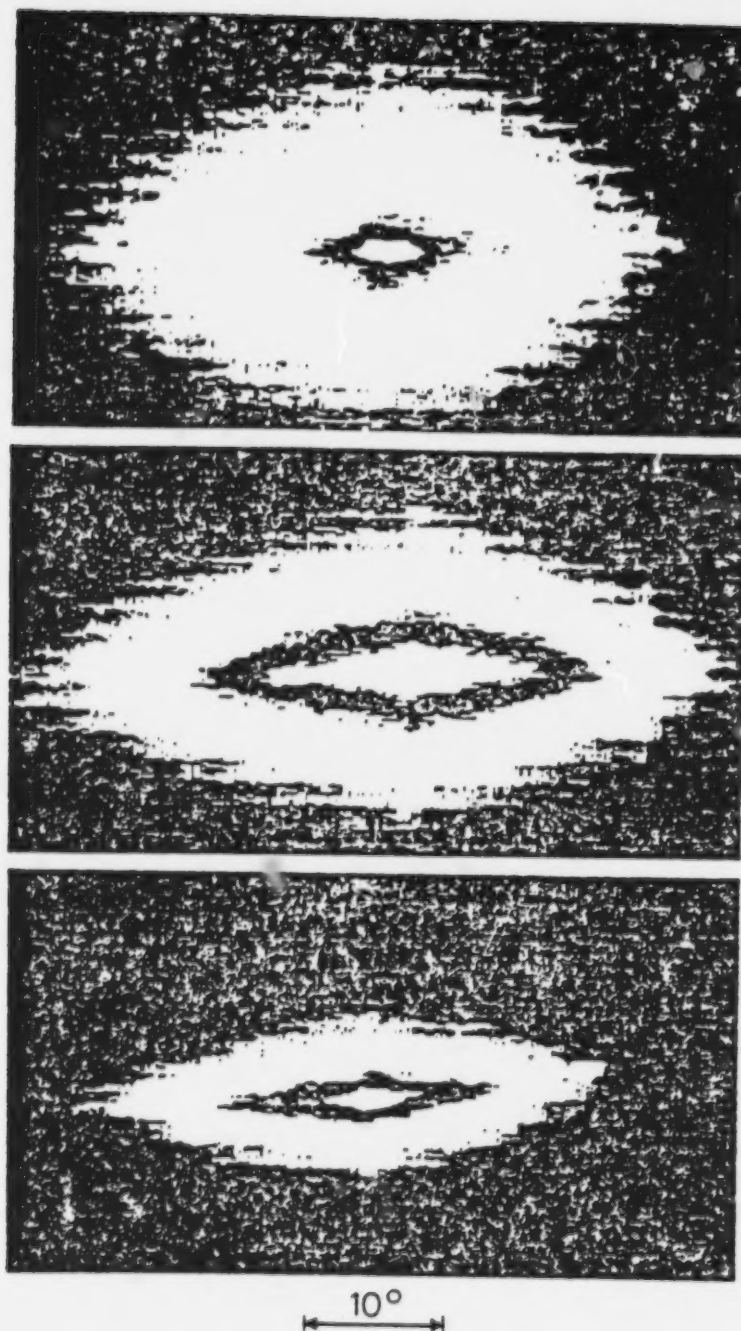


Fig. 9: Transmission light-scattering patterns obtained through the ribbons whose micrographs are shown in Figs. 6 and 7, for HSR values of (a) 1, (b) 5 and (c) 10.4

The bottom graph in Fig. 8 shows the angular deviation $\Delta\theta$ produced by the double refraction at the fiber-matrix interfaces for the values of the refractive-index ratio n_1/n_2 equal to 0.90, 0.95, 0.97 and 0.99 respectively. If the angular aperture of the detector is equal to, say, ± 5 degrees, the attenuation of the detected beam after refraction by a fiber with $n_1/n_2 = 0.90$ is seen from curve (a) of the bottom graph of Fig. 8 to amount to nearly 60% as compared to 2.7% of reflective losses. It can be concluded that refractive deviation is the preponderant mechanism for light-scattering attenuation in a medium containing fiber-like materials of refractive index close to the matrix.

If the preferentially oriented particles are neither spherical nor fiber-like, but have an intermediate shape characterized by a given aspect ratio (average ratio between their length and their diameter), the angular distribution of the light transmitted through a thin polyblend sheet may be used to evaluate such an aspect ratio. This was verified with the polyblend ribbons of different HSR whose micrographs are shown in Figures 6 and 7. The corresponding angular-scattering patterns, obtained in transmission with an apparatus of the kind shown in Fig. 1 using a He-Ne laser source, are shown in Fig. 9 for each sample. The increased elongation of the elliptical pattern obtained with higher HSR samples is evident. As explained above, such patterns can only be obtained with relatively thin films and with an appropriate sample preparation.

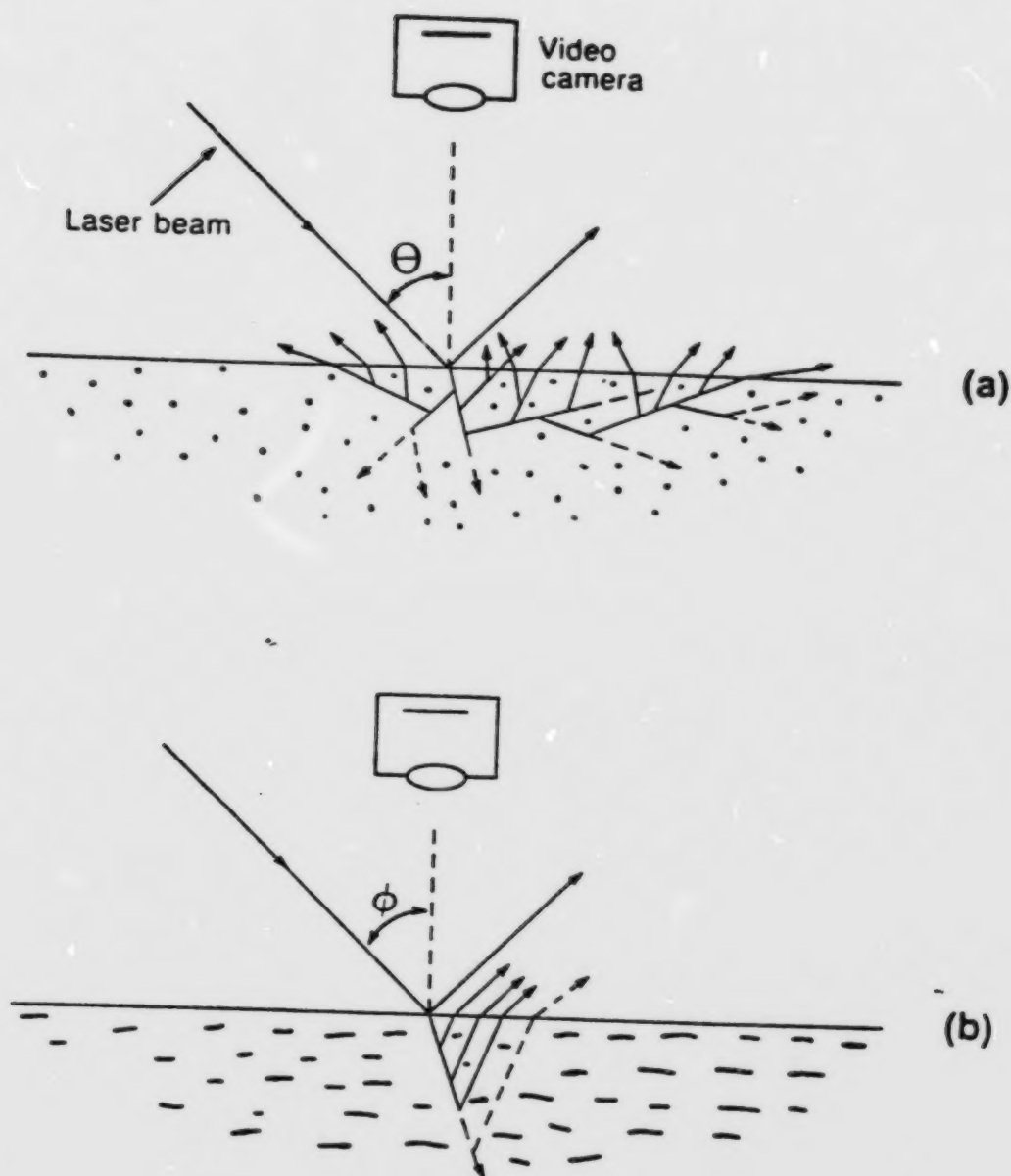


Fig. 10: Schematic diagram of light beam scattering within an oriented material for a beam incident (a) in the plane perpendicular to the fiber orientation or (b) in a plane parallel to the fiber orientation.

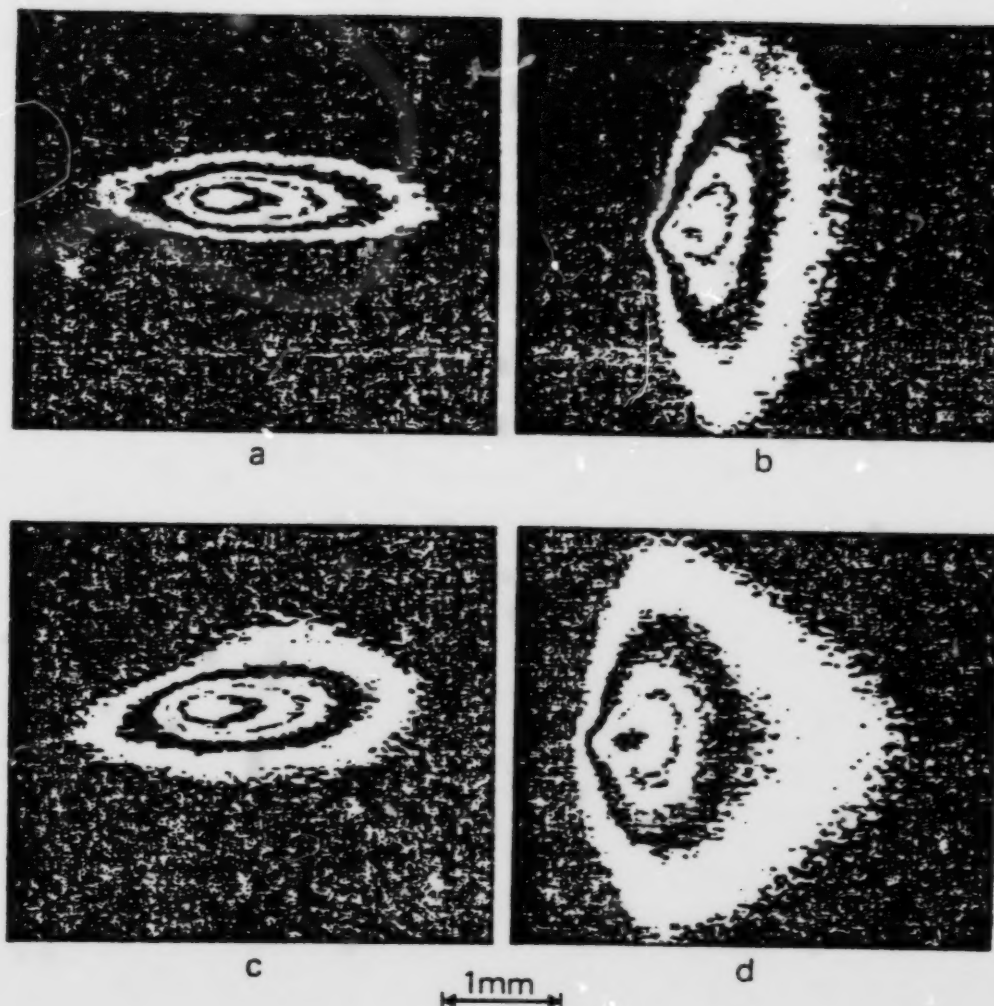


Fig. 11: Image obtained with an apparatus of the kind shown in Fig. 10 for PP/PC ribbons drawn with an HSR equal to 5 (pictures a and b) and 1 (c and d). The He-Ne laser beam was incident from the left at 45° from the normal, and the fibrillar particles in the ribbons were oriented either in the vertical (a and c) or in the horizontal (b and d) directions.

Single-side method

A single-side approach was developed for the analysis of sheets of any thickness and with little dependence on the surface finish conditions. The basic principle is illustrated in Fig. 10 in the case of a polyblend containing fiber-like particles parallel to the sheet surface and oriented in a direction (a) perpendicular and (b) parallel to the plane of incidence of the laser beam. It can be understood from such a diagram that the incident beam is preferentially scattered in the plane θ perpendicular to the fiber direction. Moreover, light scattered by the fibers in the plane ϕ parallel to the fiber direction will hardly be intercepted by the camera aperture. A directional pattern elongated in the θ plane is thus expected when the illuminated volume is imaged by the camera.

Fig. 11 shows some examples of the pictures seen by the camera in the case of the above mentioned PP/PC ribbons of HSR=5 (pictures a and b) and HSR=1 (pictures c and d). In all cases the laser beam was incident from the left, at 45° from the normal, and the fiber-like particles were oriented in a vertical (a and c) or in a horizontal direction (b and d) in the plane of Fig. 11. In other terms, the plane of incidence of the laser beam was perpendicular to the fiber orientation (direction of incident beam $\theta = 45^\circ$, $\phi = 0$) for pictures (a) and (c), while corresponding to the ϕ plane containing the fiber direction (laser beam at $\theta = 0$, $\phi = 45^\circ$) for pictures (b) and (d). The elongation of the scattered-light pattern in a plane perpendicular to the fiber orientation, as discussed with reference to Fig. 10, is evident in the images shown in Fig. 11.

The elongation and the direction of orientation of the particles in a polyblend material can clearly be inferred by an analysis of pictures of the kind shown in Fig. 11. It should be stressed that pictures such as (a) and (b) in this figure should be identical if the material were isotropic. By comparing Figs. 11 a and b with c and d we can see that the directionality of the patterns tends to disappear as the HSR, and thus the aspect ratio of the fiber-like particles, is reduced.

Analysis of thick plates

As mentioned above, one of the advantages of the one-side imaging approach as compared to through-transmission angular scattering is the possibility to inspect in-situ relatively thick materials, such as molded parts, without requiring a previous procedure of slicing thin samples, inserting them in an index-matching cell illuminated by a parallel laser beam and analyzing the angular scattering pattern. Such a potential has been verified using an apparatus of the kind shown in Fig. 10 on 3 mm-thick PP/PC plates which were prepared on a 70 ton Engel reciprocating screw injection moulding press. The temperature of the mould was maintained at 50°C. The temperature in the barrel was 250 (nozzle)/240/235/230°C. The holding pressure was 80 psi, the back pressure 300 psi and the holding time approximately 15 seconds.

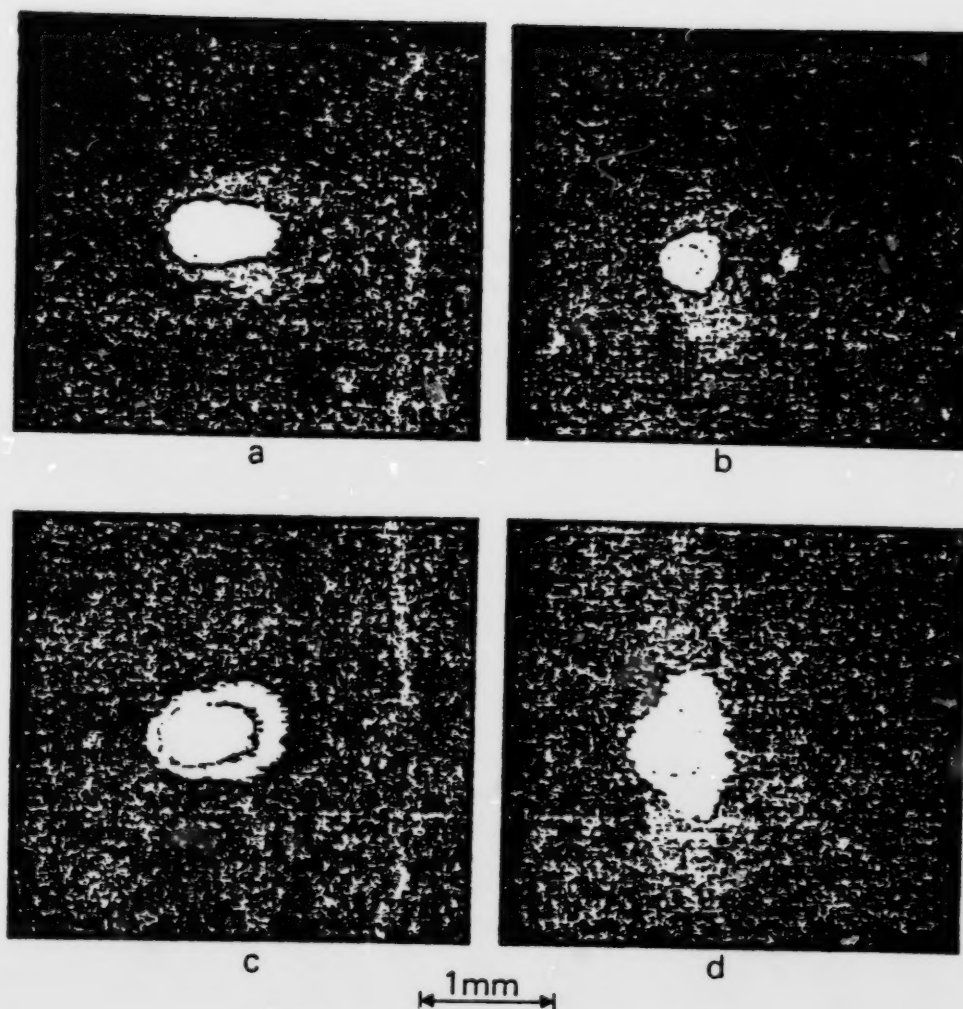
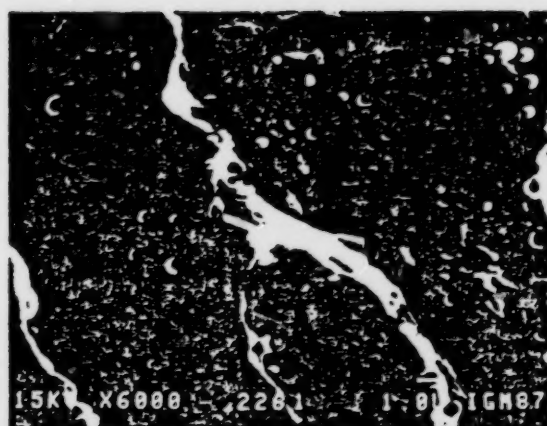
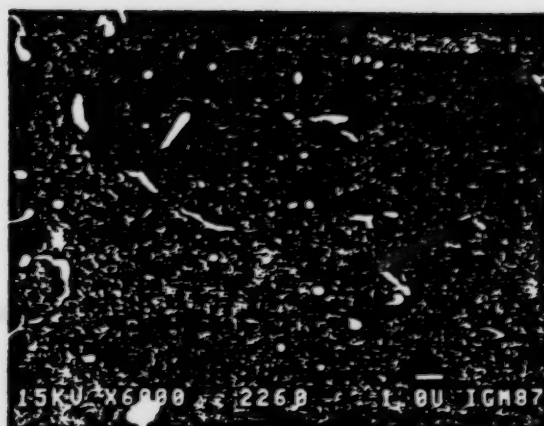


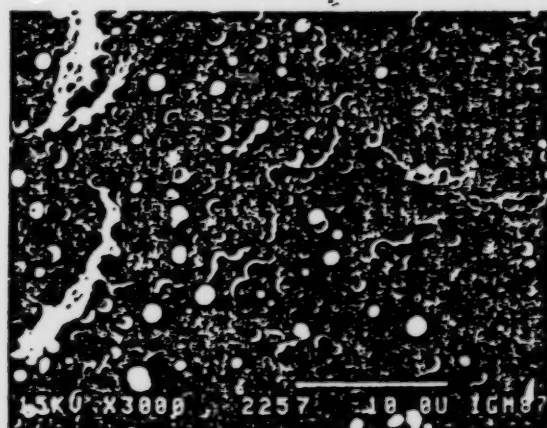
Fig. 12: Images obtained with the apparatus shown in Fig. 10 on injection moulded, 3 mm-thick PP/PC samples with 5% (pictures a and b) or 16% (c and d) PC volume concentration. The PC particles were oriented either in the vertical (a and c) or in the horizontal (b and d) direction.



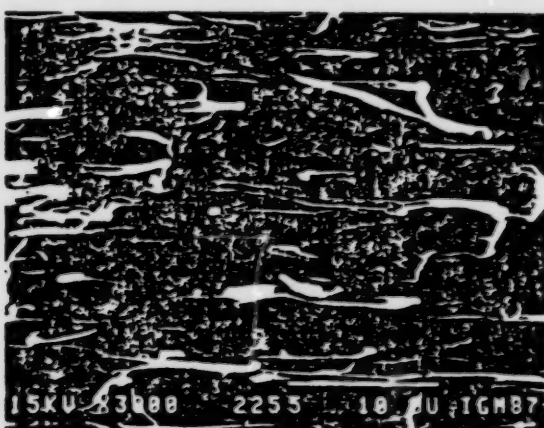
a



b



c



d

Fig. 13: Electron micrographs obtained on longitudinal sections of the 5% (pictures a and b) and 16% (c and d) PC volume concentration samples whose light-scattering patterns are shown in Fig. 12. Pictures (a) and (c) were taken in the center, whereas pictures (b) and (d) were taken near the edge of the samples.

Fig. 12 shows some examples of the pictures obtained with two plates of different PC concentration when the particles are oriented in a direction either perpendicular (pictures a and c) or parallel (b and d) to the plane of incidence (as usual, the He-Ne laser beam is incident from the left at 45° to the surface normal). The difference between the images obtained for the different fiber orientation is still noticeable, particularly near the center of the illuminated pattern. Such a difference is however less striking than in the case of Fig. 11, partly because of the random-spread effects produced by the relatively large thickness of material below the illuminated spot, and partly because of the lower degree of elongation of the PC particles in the case of these relatively thick materials. This can be seen from the micrographs shown in Fig. 13.

The photographs displayed in Fig. 13 are in the longitudinal direction fractured parallel to the direction of injection after immersion in liquid nitrogen. At a volume concentration of 5% spheres, ellipses and some fibers are noted near the edge of the sample, whereas at the center spherical particles are observed. At 16% PC more significant fiber formation is noted near the edge with spherical morphology observed in the center of the sample. The overall degree of ellipticity of the particles is much less pronounced than in the case of the extruded ribbons whose micrographs are shown in Figs. 6 and 7. This is in agreement with the lower degree of directionality of the light-scattering patterns obtained with the injection-moulded samples, Fig. 12, as compared to the corresponding patterns obtained with the extruded ribbons, Fig. 11. It should be mentioned that the particle diameters are not always larger than the

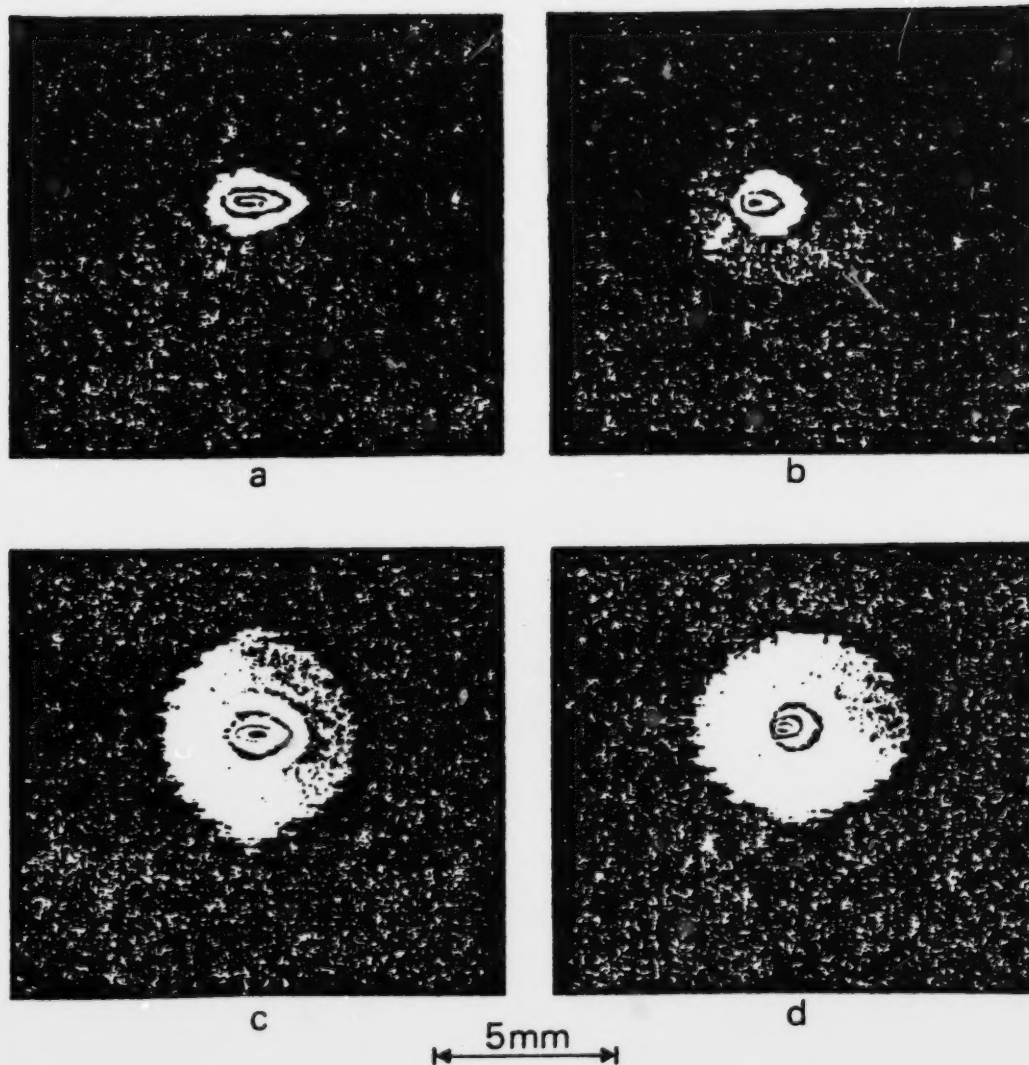


Fig. 14: Images obtained with the same samples as for Fig. 12, but with a higher light throughput and a larger optical magnification.

He-Ne laser wavelength for the injection-moulded samples, Fig. 13. More quantitative results should be possible in this case using a light wavelength in the blue or in the near-UV end of the spectrum.

Finally, it was mentioned above that the degree of directionality of the light-scattering patterns obtained for the injection-moulded samples is more pronounced near the center of the illuminated pattern. This is more clearly evident in the pictures shown in Fig. 14, corresponding to the same samples as for Fig. 12, but taken with a larger scale and higher camera sensitivity. Such a behaviour is in agreement with the electron-micrograph inspection, Fig. 13, showing that a higher degree of particle elongation is visible near the upper edge, whereas nearly-spherical particles are mainly present in the center of the sample. The part of the beam penetrating deep within the sample is scattered by essentially spherical particles into a nearly-isotropic pattern. This may suggest the possibility of a certain degree of depth-resolved directional analysis by analyzing the shape of the scattered pattern at gradually larger distances from the laser-incidence spot. A similar principle was recently put in evidence in the thermographic analysis of filler directionality in fiber-filled composites (30). Such an analysis would be an interesting approach to explore in future work.

CONCLUSION

Different light-scattering techniques have been investigated as potential candidates for the on-line characterization of polyblend materials. In general, the light-scattering approach is convenient for the characterization of polyblend mixtures with components having different refractive indices and with a limited amount of light-absorbing pigments resulting in Kubelka-Munk scattering coefficients smaller than the corresponding absorption coefficients. The optical approach is quite attractive for on-line applications because of its noncontact nature and the availability of increasingly rugged, performant and inexpensive optoelectronic devices. Particular emphasis has been given in this work to the development of techniques requiring no sample preparation and applicable to materials of realistic thicknesses, an essential requirement for on-line continuous quality control applications.

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OXYGEN PERMEATION OF BLENDS OF COPOLYMERS OF
SILOXANES AND POLY(METHYLMETHACRYLATE)

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ABSTRACT

A series of low molecular weight (≈ 40000) copolymers of methylmethacrylate, (MMA) and 4-(methacryloyloxy)butylpentamethyldisiloxane, (MBPD) have been synthesized by free radical polymerization in dimethylformamide solution. The microstructure, as derived from ^{13}C NMR spectra, indicates that the copolymers are about 80% syndiotactic with an overall random distribution ofmers. At room temperature, copolymers rich in MMA are clear, rigid glasses but become liquid at high MBPD content. Blends of these copolymers with PMMA are all heterogeneous with visible phase separation over most of the composition range. Differential scanning calorimetry studies show the presence of two T_g 's when the relative concentration of PMMA to copolymer is high. Blends of copolymers of similar siloxane content produce clear films with no indication of phase separation. The permeability to oxygen at 25 °C increases from 6.1×10^{-11} for pure PMMA to 9.1×10^{-10} (cc.

cm)/(cm² s·cm Hg) for a copolymer of MMA/MBPD of the mole ratio of 3:1. Evaluation of the permeation behaviors of the blends suggests that blends rich in siloxane exist as a layered structure with the PMMA rich component dominating the observed permeability.

INTRODUCTION

The blending of polymers is an important technological method for the production of polymer "alloys" that incorporate the characteristics of the individual blended polymers to produce a material that, hopefully, will exhibit enhancement of properties and economics. Contact lenses are one application where blending may produce a product with improved performance (1). In this case, the properties sought of the material are clarity, high oxygen permeability, hydrophilicity and good dimensional stability.

The early contact lenses, the so called "hard" lenses, were made from polymethylmethacrylate (PMMA) (2). Since the oxygen permeability of PMMA is very low, the lenses were constructed so as to act as a pump that transported oxygen rich tears to the corneal surface under the lens. The next development was lenses that were composed primarily of polymers with polydimethylsiloxane (PDMS) backbones (3). These materials have high oxygen permeability but suffer from the highly hydrophobic nature of the PDMS and the tendency to adsorb the lipophobic components of tears. Within the past ten years, a new type of contact lens has emerged. This lens is composed of a copolymer of methylmethacrylate (MMA) with a methacrylate containing a pendant siloxane group, such as 1,3-(4-methacryloyloxybutyl) tetramethyldisiloxane (4). Improvements to this basic polymer have consisted mainly of attempts to enhance the wettability and

permeability by blending with other materials and by chemical modification of the chains.

An investigation into the properties of silicone-acrylate copolymers and blends has been reported from this laboratory previously (5). Preliminary studies on blends of PMMA with poly[4-(methacryloyloxy)butylpentamethyl-disiloxane] (PMBPD) and copolymers of MMA and MBPD suggested some miscibility was occurring when both components contained a siloxane pendant group. A key question is whether there is any interaction between the PMMA backbones or the siloxane pendant groups of one blended component with that of another which can induce compatibility of mixtures of these materials. The current work uses oxygen permeability as a probe into the nature of these interactions.

GAS PERMEATION IN POLYMER BLENDS

The permeation of a molecule through a polymer film is intimately dependent on the nature of the micro and macroscopic interactions involved. At the molecular level, diffusion is dependent on the segmental motion of the chains and the resulting rapid redistribution of the free volume. Diffusion may be considered to have a kinetic dependence (rate of diffusion) and a thermodynamic dependence (solubility) according to (6)

$$P = D \cdot S \quad (1)$$

where P is the permeability, D the diffusion and S the solubility coefficient, respectively.

In an ideal, compatible polymer blend the segmental mobility of the polymer chains will be cooperative and the permeation may be considered to be a weighted average of that of the individual components. The permeation through phase separated blends will be influenced to a large degree by the morphology of the phases and the interface between them. In the extreme case one component can be considered to be completely nonsorbing and thus act as a filler in a conducting polymer matrix.

Maxwell (7) developed a relation for electrical conduction which, by analogy, can be related to gas permeation through a polymeric material. The relation defines the path length for conduction through a composite filled with nonconducting spherical particles:

$$r = 1 + \phi_d / 2 \quad (2)$$

where ϕ_d is the volume fraction of the nonsorbing species and r is the tortuosity factor, defined as the ratio of the effective path length for diffusion divided by the composite thickness. An approximation for the permeability of a composite as a function of tortuosity has been proposed by Michaels and Bixler (8) and Barrer (9);

$$P_c / P_m = \phi_m / r \quad (3)$$

where the permeabilities of the composite and matrix are given by the subscripts c and m, respectively. Combining equations (2) and (3) yields the expression for the effect of spherical, nonconducting particles on the overall permeability of a composite as

$$P_c / P_m = \phi_m / (1 + \phi_m / 2) \quad (4)$$

The requirement of the nonsorbing nature of the filler may be eliminated and an equation describing the permeation of a sorbing material in a polymer matrix has been reported by Robeson (10) as

$$\frac{P_c}{P_m} = 1 + \left[\frac{(F + 1) (P_d/P_m - 1) \phi_d}{(P_d/P_m + F) - (P_d/P_m - 1) \phi_d} \right] \quad (5)$$

where P_d and P_m refer to the permeabilities of the dispersed phase and matrix, respectively; and F is a shape factor. When $F = 2$ the equation reduces to Maxwell's relation for spherical particles and when $F = 1$ the equation becomes Rayleigh's relation (11) for cylindrical particles. If the dispersed phase is nonconductive the equation reduces to equation (4).

These equations are appropriate for a continuous contribution of gas permeation of one phase, the matrix, to the overall composite permeability. This has been extended by Robeson for the case where both phases contribute equally to the continuous and discontinuous nature of the blend. In this case there is a weighted average contribution to the total permeation from each component according to

$$P_c = x_1 P_1 \left[\frac{P_2 + 2P_1 - 2\phi_2(P_1 - P_2)}{P_2 + 2P_1 + \phi_2(P_1 - P_2)} \right] + x_2 P_2 \left[\frac{P_1 + 2P_2 - 2\phi_1(P_2 - P_1)}{P_1 + 2P_2 + \phi_1(P_2 - P_1)} \right] \quad (6)$$

where x_1 and x_2 are the mole fractions of component 1 and 2, respectively. When the contributions of each component to the continuous phase are equal a phase inversion will be exhibited.

Two additional models, described by Robeson, cover the extreme cases of permeability, i.e. the series model, for which

$$P_c = P_1 P_2 / (\phi_1 P_2 + \phi_2 P_1) \quad (7)$$

and the parallel model, for which

$$P_c = P_1 \phi_1 + P_2 \phi_2 \quad (8)$$

These models cover the limiting cases of complete discontinuity of phases and complete mixing of phases, respectively.

EXPERIMENTAL

SYNTHESIS OF POLYMERS

Free radical polymerization methods were used for the synthesis of PMMA and copolymers of MMA and 4-(methacryloyloxybutyl) pentamethyldisiloxane (MBPD). To obtain low molecular weight samples the polymerizations were performed in dimethylformamide (DMF) solution using 2,2'-azobis-(2-methylproprionitrile) (AIBN) as an initiator. The synthesis of MBPD monomer was reported previously (5). Three copolymers, designated as COP 1:1, COP 1:3 and COP 1:4 where the ratios refer to the nominal molar ratio of MBPD to MMA, have been synthesized. The procedure involved the distillation, under vacuum, of solvents and monomers and charging a 500 ml glass vessel with the

Table 1. Conditions for the Polymerization of VMA and Copolymerization of MMA and MBPD.

Polymer	Polymerization Solution				Yield %
	MMA (g)	MBPD (g)	AIBN (g)	DMF (ml)	
PMMA	87.2	----	0.41	174	52
COP 1:4	89.3	57.2	0.49	237	47
COP 1:3	69.7	68.4	0.39	256	44
COP 1:1	25.8	68.4	0.13	256	41

quantities of materials as reported in Table 1. The resulting solution was degassed by four freeze-thaw cycles and then polymerized in an oil bath at 100 °C for 30 minutes. The reaction mixture was cooled to room temperature and the polymer was precipitated by dropwise addition to a 10 fold excess of methanol. The resulting polymer was filtered, washed several times with additional methanol, and finally placed under a vacuum for 48 hours to remove residual solvents.

POLYMER STRUCTURE AND COMPOSITION DETERMINATION

Carbon 13 and proton NMR spectra were obtained with a Varian XL-300 NMR to determine the microstructure of copolymers COP 1:1 and COP 1:3. The spectra of the polymers were obtained at 60 °C for 10% by weight solutions in deuterobenzene, using a delay time of 3 seconds. The compositional analyses of the copolymers were made on the basis of the integrals of the proton signals for the methacrylate methyl and silyl methyls.

MOLECULAR WEIGHT DETERMINATION

The molecular weights of the polymers (M_n , M_w) were determined with a Varian Vista 402 gel permeation chromatograph using polystyrene standards and a Q factor of 41. The column used was a Waters Ultrastyrigel 10*4. The analyses were done at room temperature using tetrahydrofuran as a mobile phase.

THERMAL ANALYSIS

Differential scanning calorimetry was performed with a Perkin Elmer DSC-2C to determine glass transition temperatures for the polymers and blends. All samples were run at a scanning rate of 20 degrees per minute with nitrogen as a carrier gas and "quench" cooled for duplicate runs.

PREPARATION OF BLENDS AND FILMS.

Blends were prepared by solvent evaporation from 3% by weight solutions of the polymers and copolymers in methylene chloride. Several blends were made with compositions given in Table 3. The solvent was allowed to evaporate slowly over a period of 24 hours. Because of difficulties experienced in removing the films from a glass surface, the surface was coated with gold, using a vacuum deposition apparatus. Extremely small amounts of gold were used and the resulting "mirror" was partially transparent. When the solvent had evaporated the gold was dissolved by placing the casting apparatus in mercury, after which the film was easily removed. The thicknesses of the films were measured with a micrometer by taking 10 measurements at various points on the film. All samples showed a uniform thickness of approximately 0.3 mm with a standard deviation of the mean of less than 0.001 mm.

PHOTOMICROSCOPY

Blends of PMMA with COP 1:4 and PMMA with COP 1:3 were photographed at a magnification of 40x with a Zeiss microscope and an Olympus camera.

OXYGEN PERMEATION MEASUREMENTS

The permeabilities of the blends and copolymers were determined using a Mocon coulometric oxygen detector (Modern Controls Inc., Minn.) in a device similar to the Ox-Tran Model 100. This device consists of a cell which is separated into two chambers by the sample film. One side of the sample is flushed with oxygen and the other side with a nitrogen carrier gas. Any oxygen molecules diffusing through the film are carried, by the carrier gas, to the sensor which reacts electrochemically to produce a current that is monitored by a data acquisition system. This current is directly proportional to the mass flow rate of oxygen entering the sensor. Both the oxygen and carrier gas vent directly to the atmosphere and when the flow rates are identical there is no differential pressure across the film. This provides a means by which to test for the presence of pinholes in the sample; if the sensor value remains constant when the flow rate of the oxygen is increased the sample is void of pinholes. All samples were conditioned for a minimum of 12 hours in the apparatus with dry nitrogen passing on both sides of the film. The temperature was set at 25.0 ± 0.1 °C with a circulating water bath.

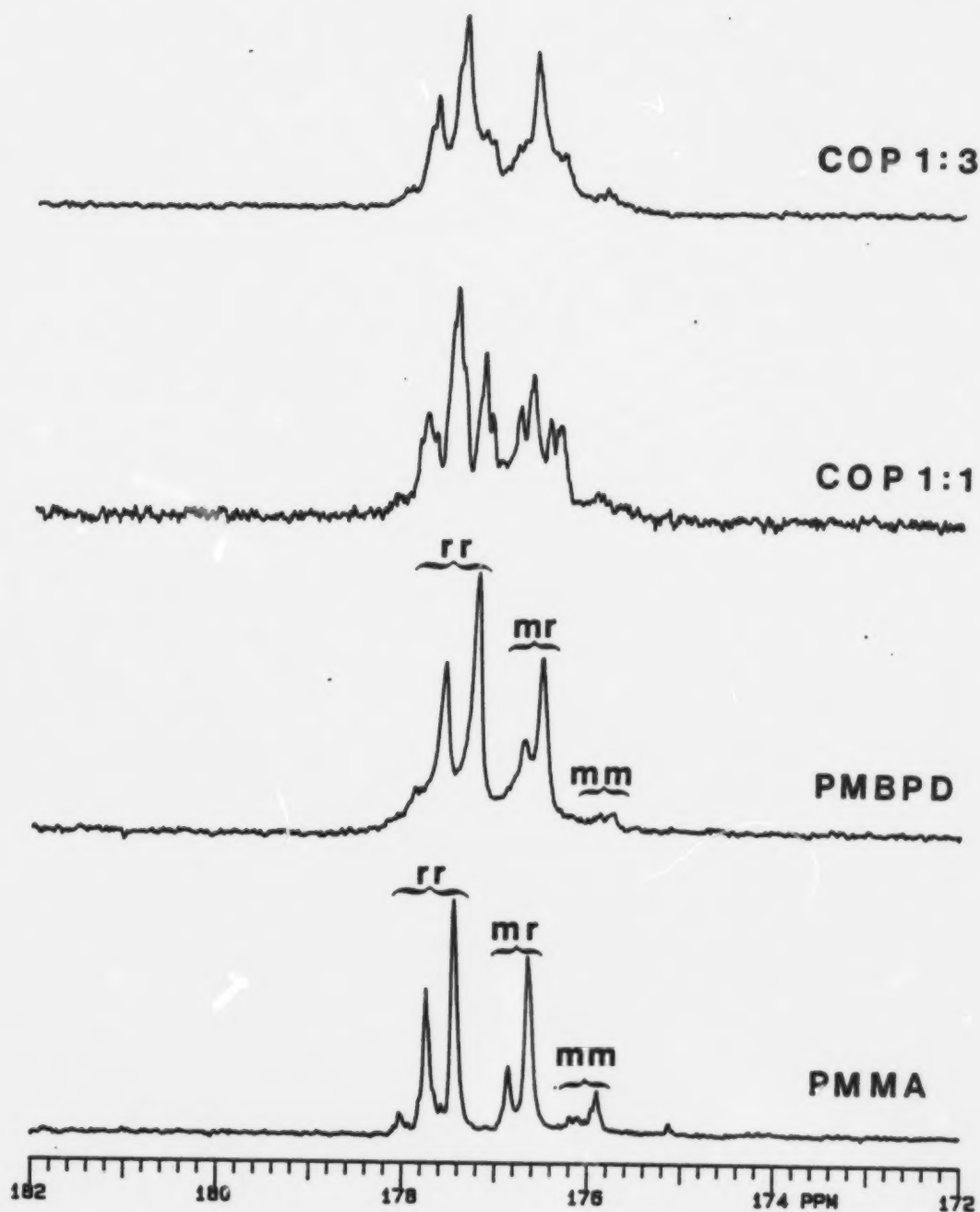


Figure 1. Proton noise decoupled ^{13}C NMR of the carbonyl regions of a) PMMA, b) PMBPD, c) COP 1:1 and d) COP 1:3.

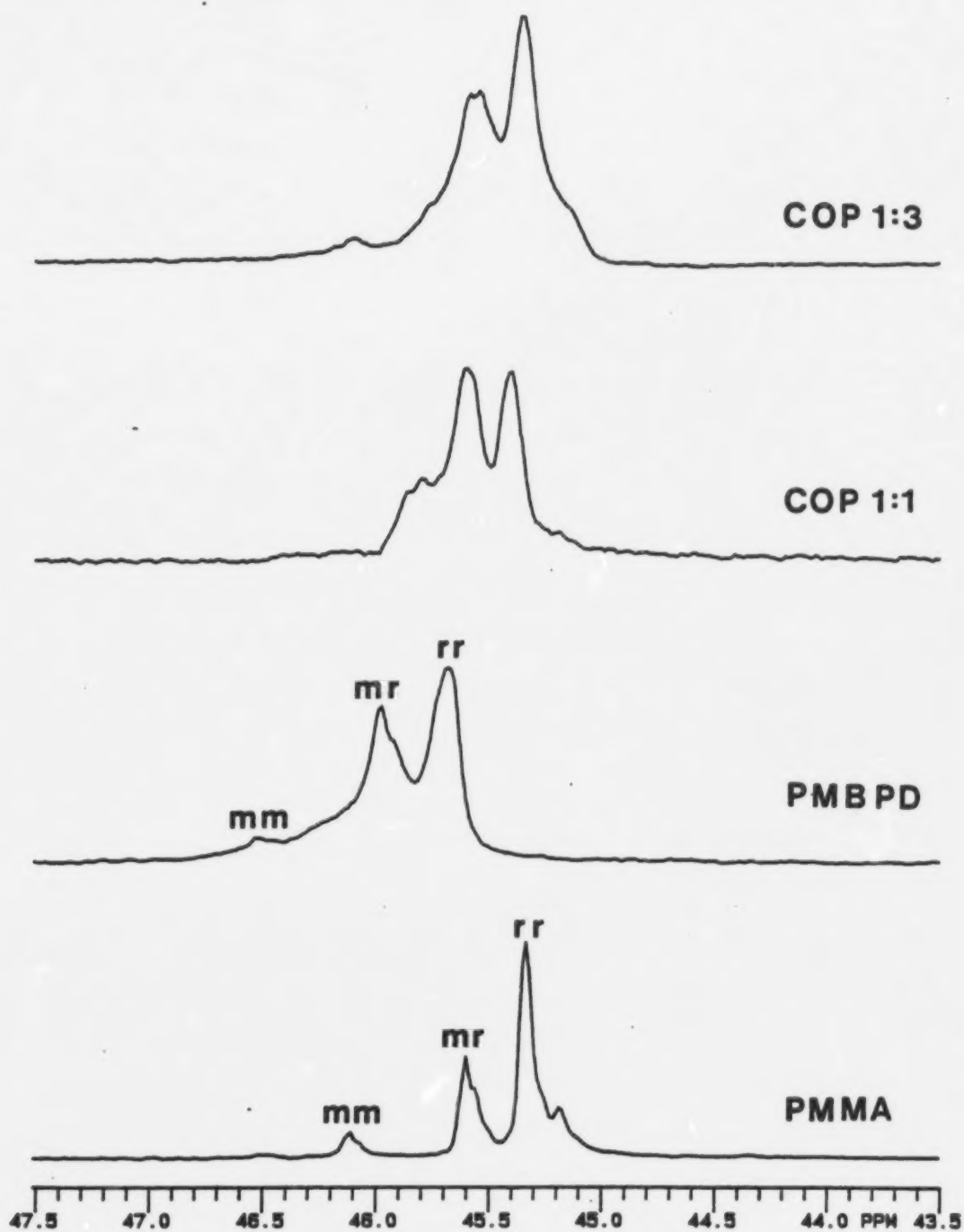


Figure 2. Proton noise decoupled ^{13}C NMR of the quaternary carbon regions of a) PMMA, b) PMBPD, c) COP 1:1, and d) COP 1:3.

RESULTS AND DISCUSSION

POLYMER STRUCTURE AND PHYSICAL PROPERTIES

The compositions and properties of the homopolymers and copolymers are listed in Table 2. The polymers are all of relatively low molecular weight and, except for COP 1:1, have T_g 's above room temperature.

Figures 1 and 2 give carbon-13 NMR spectra for PMMA, PMBPD, COP 1:3 and COP 1:1 in the carbonyl and quaternary carbon regions, respectively. Assignments for the positions of the triad fractions mm, mr, and rr, as indicated on the figures, are based on the literature assignments for PMMA (12,13). The spectra of the copolymers are consistent with an overall random distribution of mers in the polymer chains. The small additional splittings in the spectrum for COP 1:1 are indicative of random mer sequences (14).

Calculations based on integrals of the triad fractions of the spectrum (15) indicate that for PMBPD the probability of meso placement, P_m , is 0.20 and that the polymerization follows Bernoullian statistics, within, experimental error. Thus, the polymer is composed predominantly of syndiotactic triads, similar in amount to that obtained for PMMA prepared by free radical polymerization.

Inspection of the peak positions for PMBPD in the carbonyl region indicates that they are shifted upfield by 0.2 ppm relative

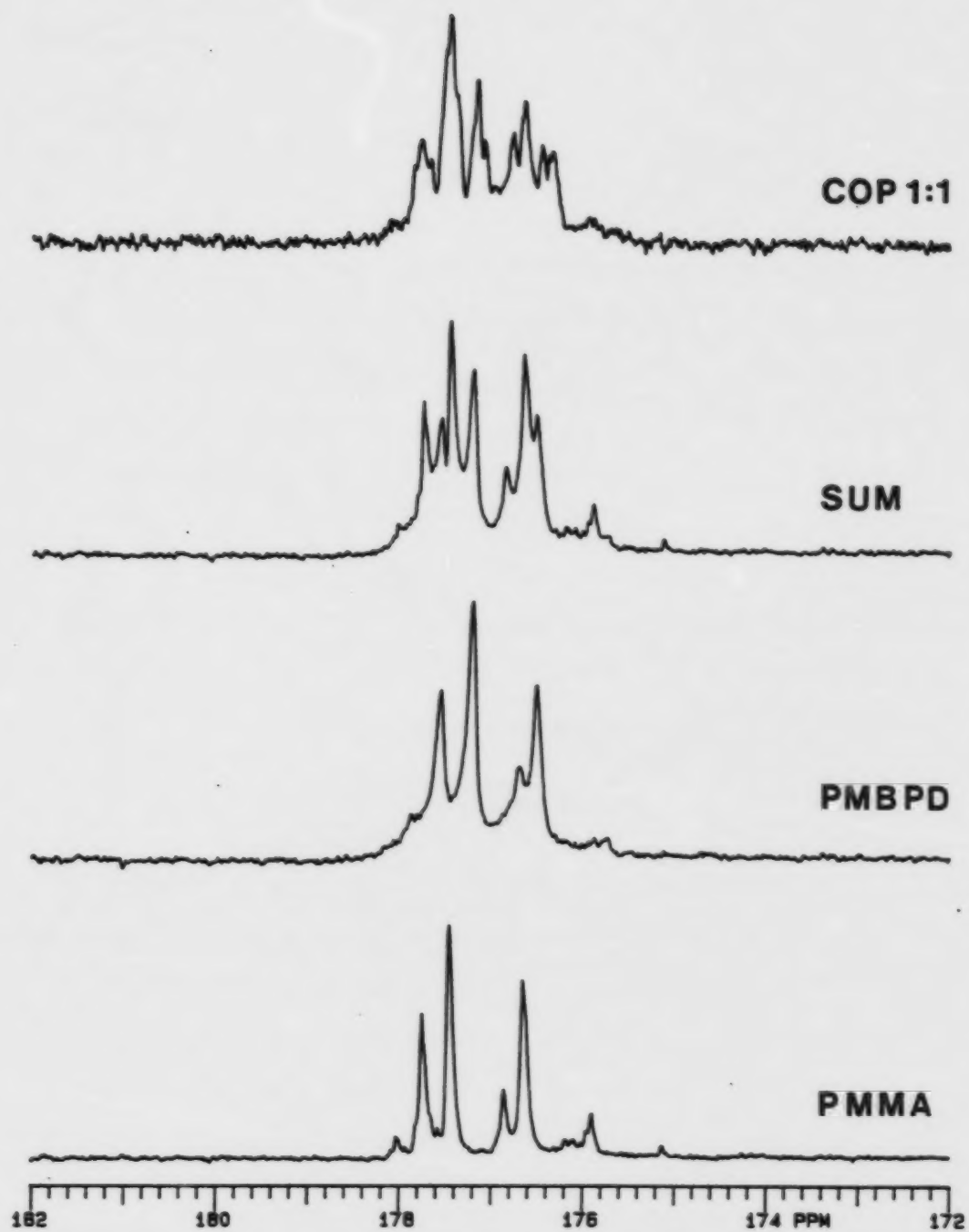
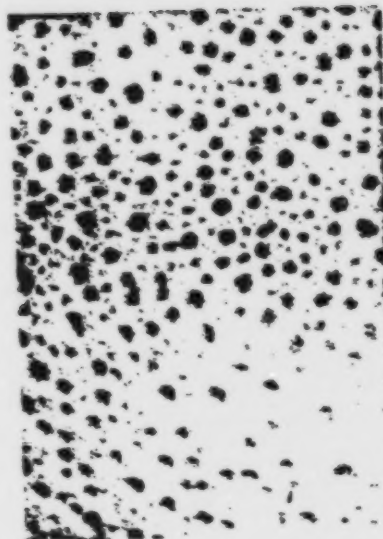
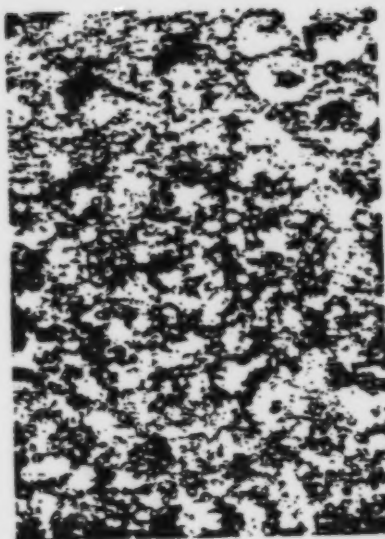


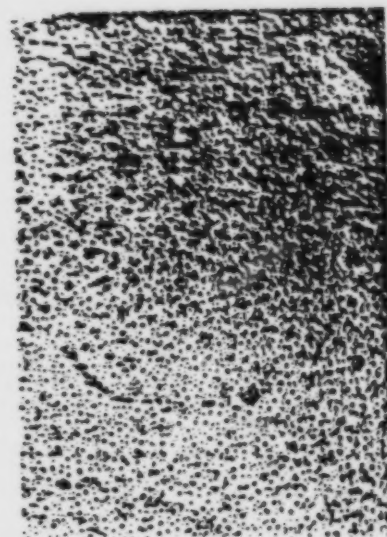
Figure 3. Computer addition of ^{13}C NMR of the carbonyl region of PMMA with PMBPD.



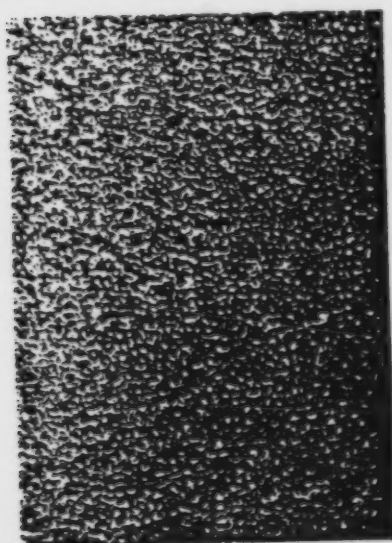
90/10



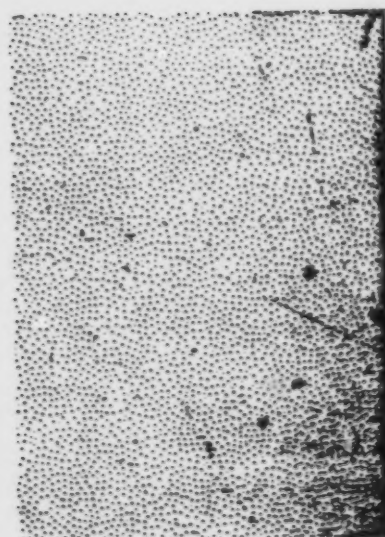
75/25



50/50



25/75

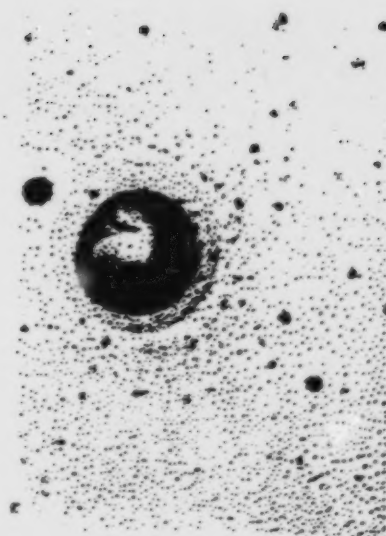


10/90

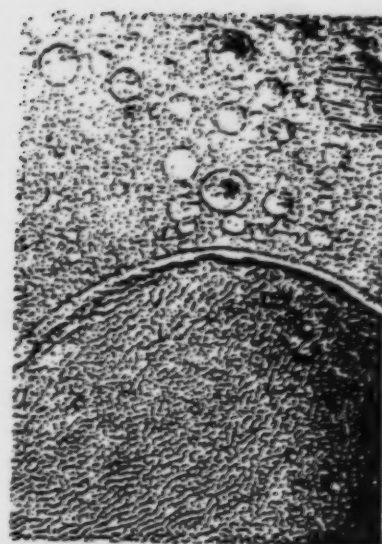
Figure 4. Photomicrographs of PMMA COP 1:4 blends at 40x magnification.
The scale of each photo is 1 by 2 mm.



90/10



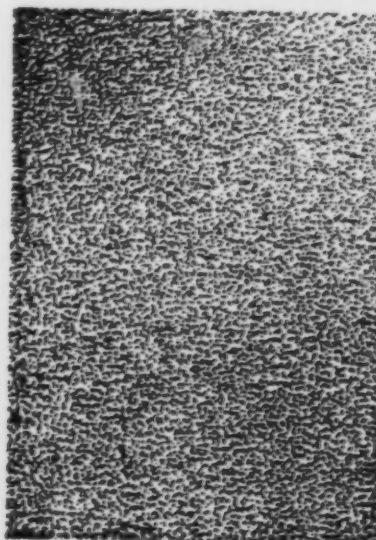
75/25



50/50



25/75



10/90

Figure 5. Photomicrographs of PMMA/COP 1:3 blends at 40x magnification.
The scale of each photo is 1 by 2 mm.

to those for PMMA. The resulting spectra for COP 1:1 and COP 1:3 are essentially superpositions of the spectra for the two homopolymers. This is illustrated in Figure 3 which contains the results of a computer simulation in which the spectra for PMMA and MBPD are added. The resulting curve is very similar to that of COP 1:1 with respect to the major peaks. Therefore, it would seem that the tacticities of the copolymers are similar to those of the homopolymers.

BLEND MORPHOLOGY

Films of excellent clarity are obtained for PMMA as well as for the copolymers. Similarly, films prepared from blends of COP 1:4 with COP 1:3 are perfectly clear at all proportions and show no evidence of opalescence, even at the microscopic level. However, this does not necessarily indicate that the polymers are completely miscible since their refractive indices are identical (1.483) so that phase separation need not necessarily be visible.

Photomicrographs of the cast films of blends of PMMA with COP 1:4 and PMMA with COP 1:3 appear in Figures 4 and 5, respectively. The field of view of each photograph is approximately 1 x 2 mm, corresponding to a magnification of 40x. Inhomogeneity is evident at all compositions for both sets of blends and it is apparent that all of the samples have some degree of phase separation. For those blends containing PMMA (refractive index of 1.492) there is a measurable difference in refractive index so that phase separation is readily detected. The most

salient feature of the photomicrographs is that at low PMMA contents, such as in the blends containing 25% and 10% by weight of PMMA (designated as 25/75 and 10/90), the domains are much smaller and are more evenly dispersed throughout the sample than those in the PMMA rich region. These small domains, presumably consisting predominantly of PMMA, appear as spherical droplets under a higher magnification and give the films a hazy appearance when viewed with the naked eye. On the basis of relative areas it would seem that there is some miscibility of PMMA with the copolymers. The samples with PMMA content greater than 50% contain domains with a range of sizes, in addition to the small droplets. This is most pronounced in the PMMA/COP 1:3 blends which show evidence of "islands" larger than 5 mm in diameter, dispersed over the entire film.

What is not apparent from the photomicrographs, due to a lack of depth perception, is that the blends that contain a concentration of PMMA of 50% and greater, in addition to the domains within the film, also appear to have droplets deposited on their surface during casting. These appear as actual raised areas on the "upper" (i.e., the surface away from the gold during casting) surface of the films and seems to indicate that the siloxane rich component tends to form a layer on the surface of the PMMA. This behavior is not apparent in the blends of 25/75 and 10/90 composition.

These observations suggest that the higher the siloxane content in the copolymer blended with PMMA, the greater the degree

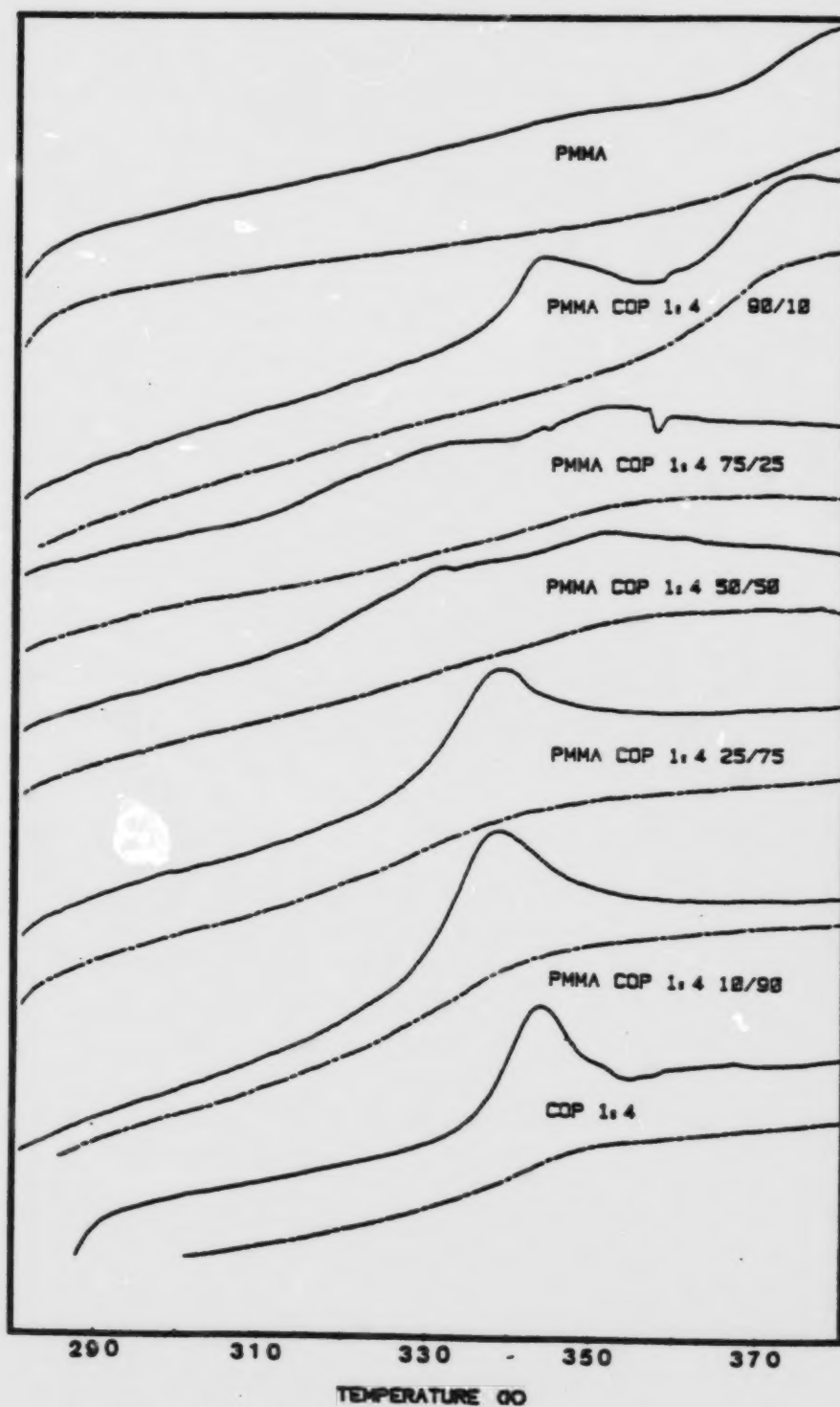


Figure 6. DSC thermograms for PMMA COP 1:4 blends. Data for each blend is shown as a pair of curves with the solid and dashed lines denoting the first and second scans respectively.

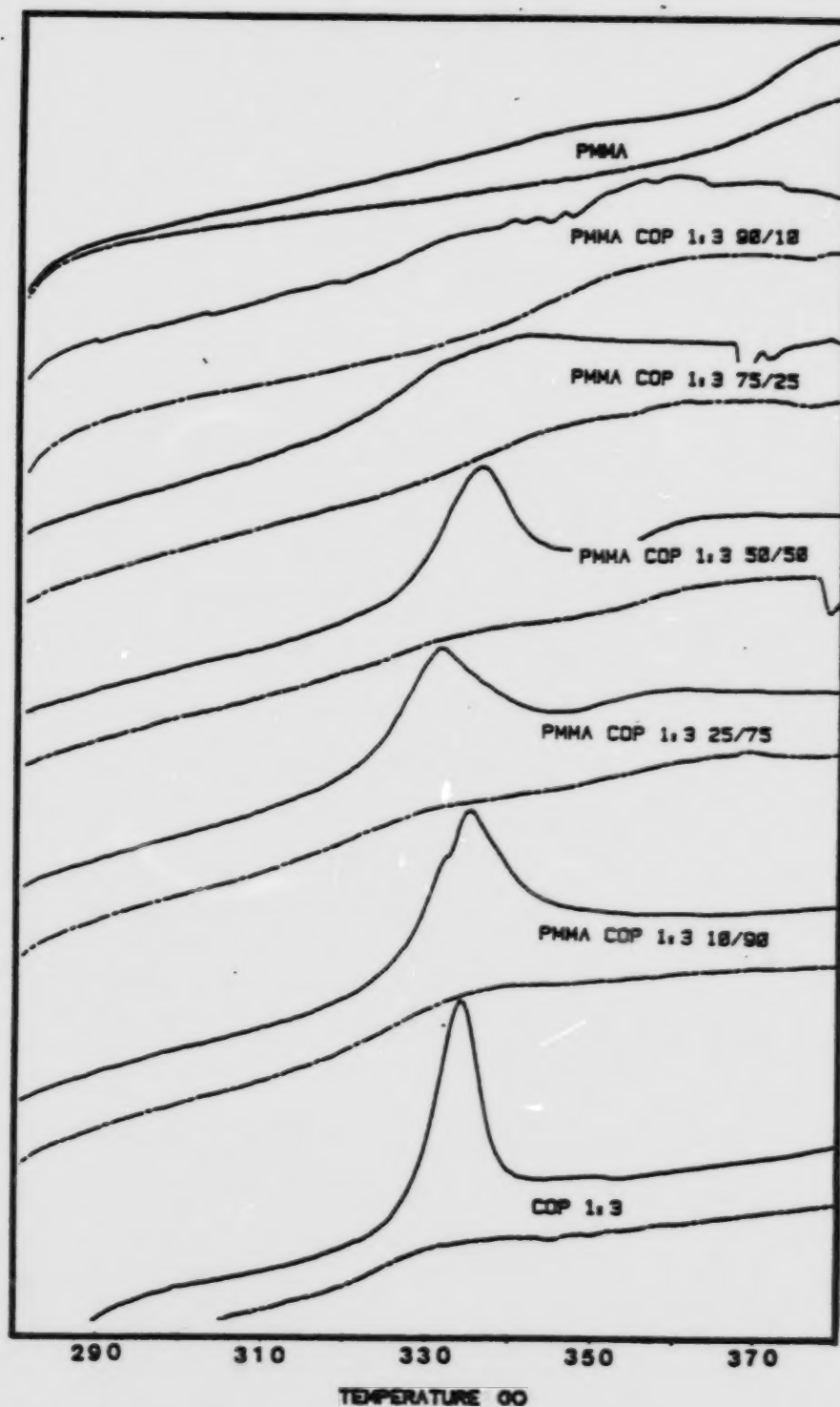


Figure 7. DSC thermograms for PMMA COP 1:3 blends. Data for each blend is shown as a pair of curves with the solid and dashed lines denoting the first and second scans respectively.

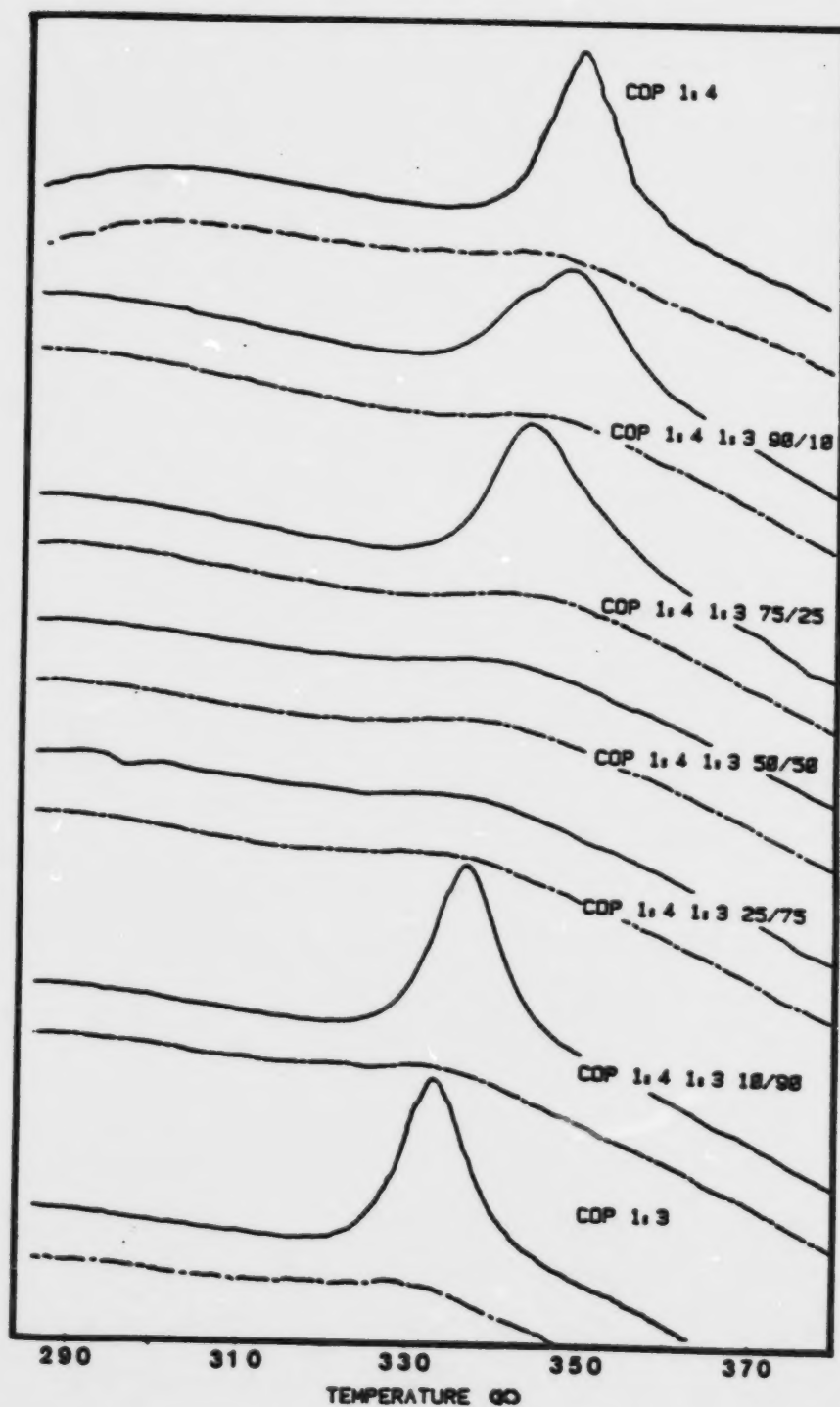


Figure 8. DSC thermograms for COP 1:4 COP 1:3 blends. Data for each blend is shown as a pair of curves with the solid and dashed lines denoting the first and second scans respectively.

of phase separation and the tendency for layer formation during casting. For the copolymers under study, the chain backbone is identical to that of PMMA while the pendant group is similar to polydimethylsiloxane (PDMS). The large differences in solubility parameter values for PMMA ($\delta = 11.0$) and PDMS ($\delta = 7.5$) (16) indicate that cosolubility is unlikely. However, depending upon relative ratios of MMA mers to siloxane mers the differences may be smaller and in the limit some cosolubility may occur.

DSC RESULTS

DSC scans of the blends of PMMA with COP 1:4, PMMA with COP 1:3 and COP 1:4 with COP 1:3 appear in Figures 6, 7 and 8, respectively. A first and second scan, after quench cooling, are presented for each sample. Tables 2 and 3 contain a listing of the approximate glass transition temperatures, T_g 's, for the various samples. Essentially equivalent results were obtained for powder samples, obtained from the original precipitation, and for film samples. The reported values are estimates of "onset" temperature based on the first scan for each sample. In certain cases this leads to difficulties in interpretation of transition temperatures. The problem relates, in part, to "frozen in" stresses, evidenced by apparent endotherms on the thermograms. This is particularly noticeable for the copolymers and for blends that are rich in either copolymer and may be related to the extraordinarily large thermal expansion coefficients evidenced by

siloxane containing polymers (17). Generally, first scans of a given sample can show shifts of a few degrees from the T_g 's determined on the second and subsequent scans (18). Unfortunately, in the case of the samples presented here, for example, blends of PMMA with COP 1:4 at compositions of 75/25 and 50/50, the second scans appear to show only a single T_g , which implies miscibility. However, as indicated by the photomicrographs, this is not an accurate indicator for these samples. Heating the sample above its T_g in an oven causes little change in the appearance of the film, and as expected, does not enhance miscibility.

For blends of PMMA with both copolymers the first scan reveals evidence of two T_g 's for each composition, except at 25/75 and 10/90 for the PMMA/COP 1:4 blends and a composition of 10/90 for PMMA/COP 1:3 blends. This is more apparent for the first scans than for the second scans. For the second scans only a single, broad T_g is seen at all compositions for the PMMA/COP 1:4 blends and its position is shifted away from the T_g of PMMA, which suggests at least a limited miscibility of PMMA in COP 1:4. For blends of PMMA/COP 1:3 the second scan shows two T_g 's for all compositions except, perhaps, that at 10/90. Furthermore, the position of the T_g corresponding to the PMMA decreases while the T_g corresponding to the COP 1:3 remains unchanged with increases in PMMA content.

For blends of COP 1:4 with COP 1:3 there appears to be a single, composition-dependent T_g whose midpoint shifts between that of the pure components. It is generally accepted that the

Table 2. Polymer Compositions and Properties

Molar Ratio		T_g (K)	M_N	M_W	$PO_2 \times 10^{11}$
Polymer	MBPD/MMA		$\times 10^{-3}$	$\times 10^{-3}$	(cc-cm)/(cm ² s-cm Hg)
PMMA	-----	368	23	54	6.2
COP 1:4	1:4.3	334	31	66	47
COP 1:3	1:2.8	320	37	70	91
COP 1:1	1:1.0	285	50	85	---

Table 3. Blend Compositions and Properties

Feed	Weight Ratio	T_g	$PO_2 \times 10^{11}$
			(cc-cm/cm ² s-cm Hg)
PMMA	90/10	334, 368	7.3
+ COP 1:4	75/25	?, 346	9.0
	50/50	?, 346	16
	25/75	334	31
	10/90	334	47
PMMA	90/10	20, 350	7.0
+ COP 1:3	75/25	320, 350	8.7
	50/50	320, 350	12
	25/75	320, 350	46
	10/90	320	71
COP 1:4	90/10	331	47
+ COP 1:3	75/25	328	49
	50/50	324	50
	25/75	323	55
	10/90	322	66

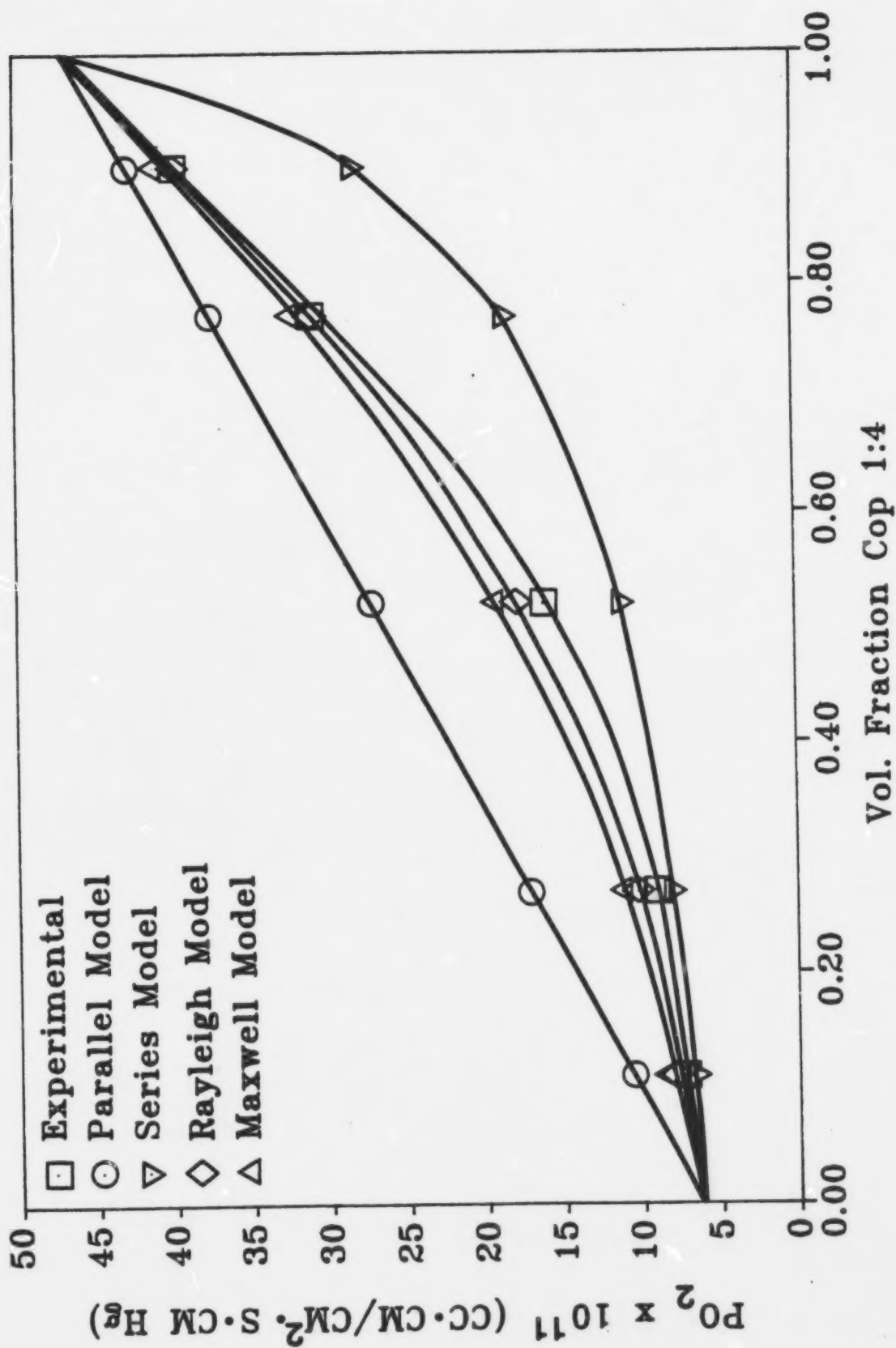


Figure 9. Experimental and model oxygen permeabilities (P_{O_2}) for PMMA COP 1:4 Blends.

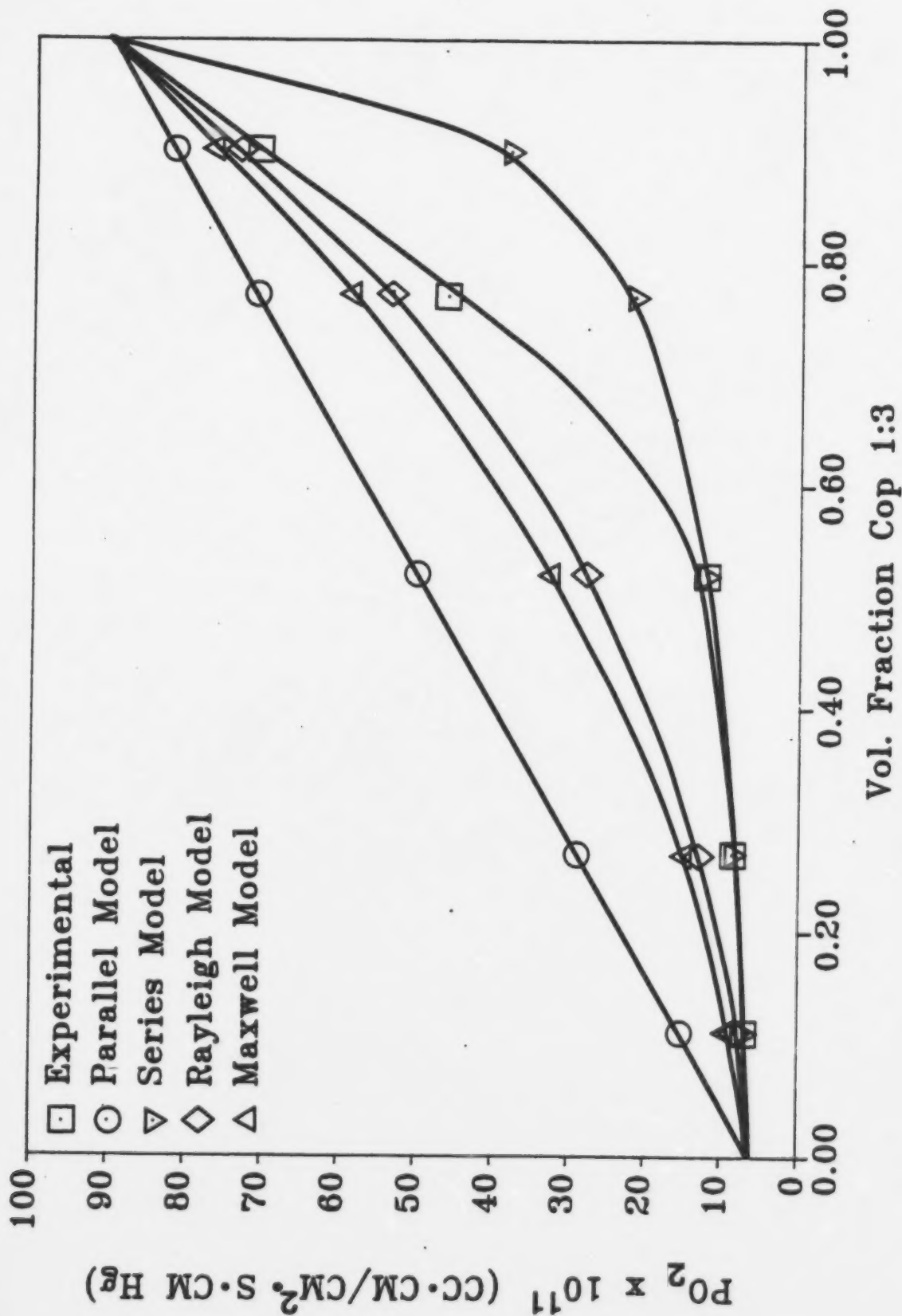


Figure 10. Experimental and model oxygen permeabilities (P_{O_2}) for PMMA COP 1:3 Blends.

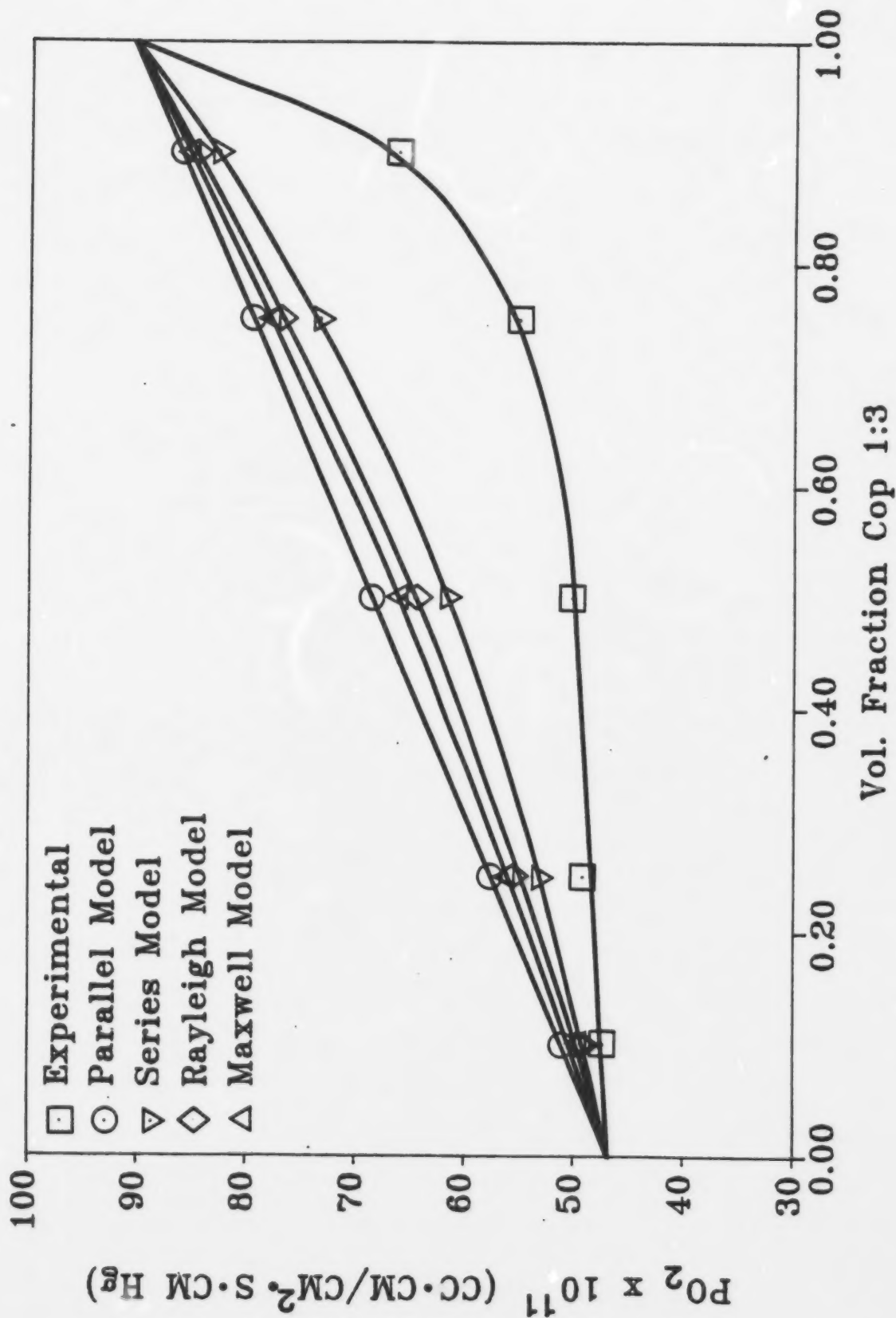


Figure 11. Experimental and model oxygen permeabilities (PO_2) for COP 1:4 COP 1:3 Blends.

presence of a single T_g is a criterion for miscibility in blends (17). However, this is not sufficient in that single T_g 's may be observed if the T_g 's for individual components are separated by less than 20 or 30 degrees. Consequently it is not certain that these blends are entirely miscible since there is a fair degree of uncertainty in these results due to the broadness of the resulting transitions and the closeness of the T_g 's of the copolymers.

OXYGEN PERMEABILITY RESULTS

The results for the oxygen permeability of the homopolymers and blends are reported in Tables 2 and 3. Intra-sample permeation determinations for the homo and copolymers as well as for the blends were reproducible to better than $\pm 3\%$ while measurements on duplicate films were reproducible to better than $\pm 8\%$. The result for PMMA films compare favorably with reported literature values of 1.0×10^{-11} (cc·cm/cm²·s·cm Hg) (1). Presumably, the small difference can be attributed to differences in sample preparation, casting methods etc. For the copolymers, it is clear that the presence of the siloxane group enhances oxygen permeability. A comparison of these values with patent literature reveals that the values are close to that of other siloxane-containing methacrylate derivatives used in contact lenses with reported oxygen permeation ranging from 13×10^{-11} to 320×10^{-11} cc·cm/cm²·s·cm Hg, depending on siloxane content (19, 20).

Plots of oxygen permeability as a function of volume fraction of blended components appear in Figures 9, 10 and 11.

Included in these plots are the curves based on calculations using the series, parallel, the modified Maxwell and the modified Rayleigh relations.

As would be expected, the blends of PMMA with the copolymers show oxygen permeation below that predicted by the parallel model. The behavior of blends with COP 1:4 (Fig. 9) approximately follows results predicted by the Rayleigh relation for composites of two permeable materials. At compositions rich in PMMA the data falls somewhat below the Rayleigh prediction, closer to the series model. The limited miscibility of copolymer in PMMA does not increase oxygen permeation, which suggests that interfacial phenomena play a role here.

The general behavior of blends of COP 1:4 in PMMA is seen in an emphasized manner for the blends of COP 1:3 with PMMA. For compositions containing less than 50% by volume PMMA the oxygen permeation clearly follows the predictions of the series model. This would seem to indicate that a "layering" effect may be occurring in which copolymer takes a conformation such that the siloxane units tend to aggregate. At higher concentrations of COP 1:3 the oxygen permeation increases dramatically so that, ultimately, the permeation again reaches that predicted by the Rayleigh relation. However, it is apparent from the photomicrographs that the blends do not adhere to the geometrical constraints used in the derivations of the models. The models were developed with specific constraints as to particle geometry (i.e. spheres in the case of Maxwell's model) and uniformity of size

and shape of domains which clearly do not exist, except possibly in the samples with a low PMMA content. In addition, the models assume that a continuity exists between phases. These samples show domains of various sizes and shapes and there are clear indications of discontinuities at the interface. None the less, there is strong evidence for a "layering" effect based on permeation that approximates the series model. A significant observation, reported previously (4), is that films of blends of PMMA with PMBPD homopolymers are perfectly clear but are coated with PMBPD, which at room temperature is a viscous liquid with a T_g of 236 K.

The oxygen permeabilities of blends of the copolymers fall drastically below those predicted by the series model. Such behavior is completely unexpected for homogeneous blends. The microphase separation referred to previously is also indicated here. This apparently leads to some "layering" effect that has a strong effect on oxygen permeability.

CONCLUSIONS

The results suggest only limited miscibility of PMMA with the MBPD copolymers, and that occurring to an appreciable extent only when the quantity of siloxane is small. Since these are random copolymers, of similar tacticity, immiscibility can be attributed solely to the presence of the siloxane pendants. Furthermore, oxygen permeation data indicate a tendency for a "layering" of the siloxane rich component on the surface of the

PMMA rich component. The permeation of oxygen through these samples is controlled to a large degree by the PMMA rich phase. This becomes more pronounced as the relative quantities of siloxane increase, both within a given series of compositions of a blend system and between the different systems.

ACKNOWLEDGMENTS

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SYMBOLS

AIBN	2,2'-azobis(2-methylproprionitrile)
C_p	Heat capacity
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
MBPD	4-[methacryloyloxy]butylpenta- methyldisiloxane
MMA	methylmethacrylate
P_b	Permeability of blend
P_m	Permeability of matrix
PDMS	Polydimethylsiloxane
PO_2	Oxygen permeability
T_g	Glass transition temperature
δ	Solubility parameter
ϕ	Volume fraction
τ	Tortuosity

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**ADDITIVES FOR IMPROVING THE STRENGTH, STIFFNESS AND DUCTILITY
OF EPOXY RESINS**

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Abstract

A range of additives at 7-20 wt% loading can increase the stiffness and strength of crosslinked epoxy resins by up to 60%, yet the tensile specimens also fail in a ductile fashion. In additive formulations where little chemical bonding occurs between the additive and the epoxy matrix (eg the reaction product of 4-hydroxyacetanilide and 1,2-epoxy-3-phenoxypropane), the increase in modulus is directly related to the decrease in free volume available for segmental mobility. The increase in strength results from a combination of the increased modulus and an increased fracture energy. A ductile mode of failure occurs because the cured plastic exhibits a large increase in free volume on straining (low Poisson's ratio). The strain-induced increase in free volume effectively takes the sample through the glass to rubber transition. In more highly reactive formulations (eg the reaction product of 4-hydroxyacetanilide and vinyl cyclohexene dioxide), chemical bonding effects complicate this simple free volume interpretation, but the occurrence of a ductile failure mode is again related to the free volume increase with strain.

Introduction

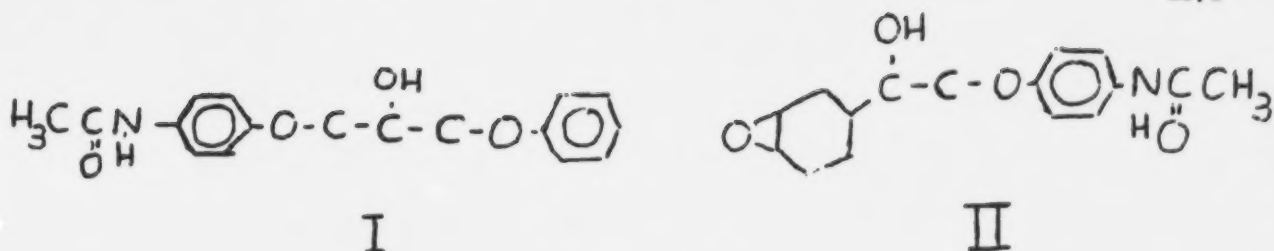
Crosslinked epoxy resins have been used for many years as adhesives, for encapsulation, for coatings, and as structural plastics. They have advantages of ease of handling, good chemical and thermal stability, and good electrical properties. However, for many structural applications the brittleness of the crosslinked plastic has limited its use, and there has been considerable research into modification of the fracture behaviour of crosslinked epoxy resins(1-3). Among the approaches which have achieved partial success are the use of higher molecular weight epoxy resins (therefore increasing the distance between crosslinks), the use of flexible curing agents (eg long chain aliphatic polyamines), and the incorporation of carboxy-terminated elastomers. None of these approaches is without its disadvantages, particularly with regard to a decrease in modulus, glass transition temperature (T_g) and resistance to hydrolytic degradation, and so we have explored alternative methods of obtaining crosslinked epoxy resins with good mechanical properties.

We have described previously a range of additives given the descriptive name "Epoxy Fortifiers"(4-7). When added to amine-cured epoxy resins at 10-20 wt% loading, these materials produce an increase in stiffness and strength of up to 60%, yet tensile test specimens also fail in ductile fashion, which has important consequences for the damage tolerance and machinability of the cured plastics. The earlier publications were concerned primarily with the effect of the additives on the modulus of the plastic. In particular, for the additive EPPHAA (the reaction product of 1,2-epoxy-3-phenoxypropane (EPP) and 4'-hydroxyacetanilide (HAA)), we demonstrated the existence of a negative volume of mixing between the additive and the polymer, a suppression of the low temperature relaxations of the polymer, and the occurrence of strong molecular interactions between the

additive and the polymer (4,7). These observations were rationalised in terms of the concept of "antiplasticisation", ie a decrease in free volume which restricts molecular mobility and hence increases the modulus. The more reactive additive formulations, eg VCDHAA (the reaction product of vinylcyclohexene dioxide (VCD and HAA) were shown to become partially chemically bonded to the crosslinked polymers, but otherwise to function in a manner similar to the less reactive formulations(5). We have also demonstrated the usefulness of these additives in producing improved matrix materials for carbon fiber and glass fiber composites (6). We give here a more generalised description of fortifier behavior, with particular emphasis on the occurrence of a ductile mode of failure under tensile stress.

Experimental Section

Full details of the synthesis of the various additive formulations are given elsewhere(4,5,7). The two additives described in detail here are the reaction product of 1,2-epoxy-3-phenoxypropane (EPP) and 4-hydroxyacetanilide (HAA), called EPPHAA, and the reaction product of vinylcyclohexene dioxide (VCD) and HAA, called VCDHAA. EPPHAA was prepared by heating EPP and HAA at a 1.05:1 mole ratio to 160°C for 60 minutes in the presence of 0.1 wt% diethylamine hydrochloride catalyst(4). VCDHAA was prepared by heating VCD and HAA in a 1.2:1 mole ratio to 120°C for 60 minutes in the presence of 0.1 wt% diethylamine hydrochloride catalyst(7). These materials are low melting point solids, which are mixed with the resin and curing agent just prior to use(4-7). Typical additive levels are 5-20 wt%, ie 7-30 parts per hundred parts of resin (phr). The major components of EPPHAA and VCDHAA have the structures described below (I and II respectively.)



The epoxy resin system used to obtain the data presented here comprised a diglycidyl resin (Epon 828, Shell) and an aromatic amine curative (Diaminodiphenylmethane, DDM, Ciba-Geigy HT972) at 30 phr. However, the additives have also been shown to be beneficial in a wide range of other epoxy systems(5,7). The uncured epoxy system was poured into stainless steel molds and subjected to a cure cycle of 3h at 100°C and 3h at 150°C, followed by a slow cool down step at <1°C/min. The cured plastic was machined into tensile "dogbones" to conform to ASTM D638, type II, for tensile testing at 25°C and 2% min. Tensile strain was measured with a clip-on Instron strain gauge, Fracture toughness K_{IC} measurements were made using rectangular compact tension specimens as described by Ting and Cottingham(9). The volume changes accompanying the application of tensile stress were measured using perpendicularly aligned glue-on strain gauges. The data are expressed as volume expansion, not as Poisson's ratio as is conventional in metals technology, because the samples respond to stress in a viscoelastic fashion, which therefore makes Poisson's ratio a time dependent variable. The volume changes accompanying an increase in temperature were measured with a thermomechanical analyser (Dupont 910 TMA). Specimens were annealed in the TMA at $> T_g$ to remove frozen-in mechanical stresses associated with cutting the sample, then cooled in the TMA cell at controlled rates. To examine the effect of thermal history on the physical and mechanical properties of the cured plastics, several specimens were

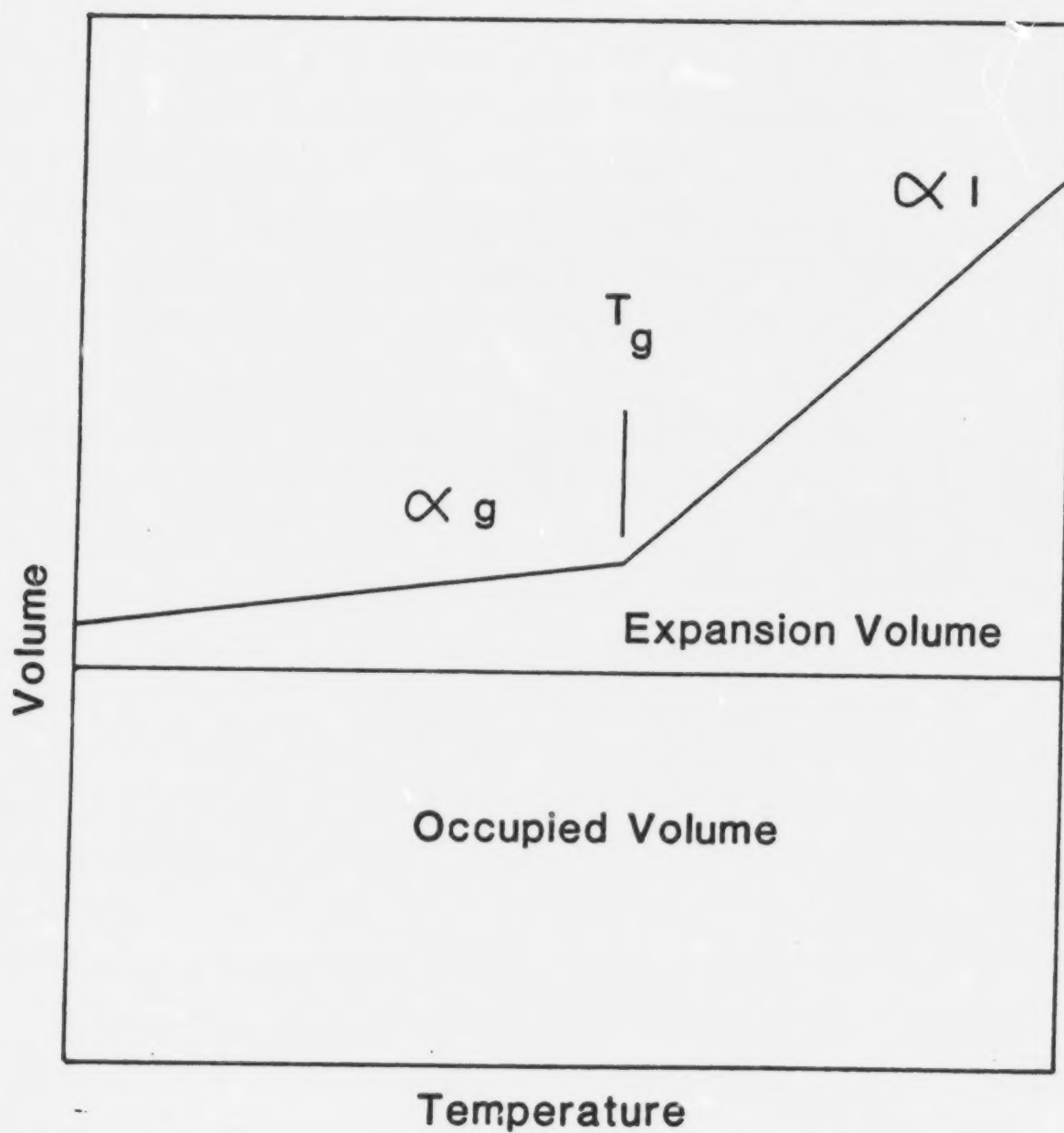


Figure 1 A schematic representation of the free volume of a polymer.

removed from the cure oven at the end of the cure cycle and cooled at controlled rates of up to 30°C/min. The cooling rates were monitored by embedded thermocouples.

Free Volume Model of Ductile Failure

The concept of "free volume" has been used for many years to describe the mobility of additives in polymers and to describe the mobility of segments of the polymer itself(10). Briefly, a certain portion of the volume of a polymer may be considered as unoccupied by the polymer molecules and so is freely accessible either to additive migration or self diffusion of the polymer chain segments. The physical and mechanical properties of polymers, which depend on the ability of the polymer chains to move in response to external stress, therefore will be strongly dependent on the free volume.

Free volume is generally treated as a semi-quantitative concept which is more useful for the rationalisation of phenomena than for quantitative prediction of polymer properties. However in this case, where there is a strong emphasis on dilatometric measurements, a free volume approach is useful quantitatively. There are several ways to quantify the free volume of a system. Conceptually, one of the simpler interpretations of free volume is based upon the expansion volume (V_E), ie the amount by which the volume exceeds that of a crystalline form of that material (V_0) at 0°K (Fig 1), ie

$$V_E = V_T - V_0 \quad (1).$$

There has been extensive study to calculate and/or measure values of V_0 for common polymers. These usually involve either the measurement of crystalline densities at low temperatures, or the use of additivity relations for certain atomic volume parameters(10,11). For the analysis described

below, no absolute value of V_0 is required, but it should be recognised that V_E will not be zero at 0°K because of imperfect packing of the polymer glass. With increasing temperature V_E increases with an expansion coefficient α_g , until the glass transition temperature (T_g) is reached, after which V_E increases more rapidly (expansion coefficient α_l). Typical values of V_E for polymers are 12-15%. Undoubtedly this is an overestimate of the true free volume available for segmental diffusion, because not all the extra space generated by thermal motion will be accessible to other segments. Therefore, a correction factor (β) is introduced to allow for the increase in molecular dimensions with increasing temperature. This correction factor was equated by Rusch and Beck(11) with the difference in expansion coefficients of the glass (α_g) and the ideally crystalline material (α_c). The free volume of the system (V_f) at $T < T_g$ therefore is:

$$V_f = \beta V_E = \left(\frac{\alpha_g - \alpha_c}{\alpha_g} \right) V_E \quad (2)$$

The application of a tensile stress will also produce an increase in volume, because Poisson's ratio (μ) for polymeric glasses is less than 0.5. The volume increase (ΔV_{strain}) between strain zero and ϵ is:

$$\Delta V_{\text{strain}} = \epsilon(1-2\mu) \quad (3)$$

Not all the extra volume produced by strain will be accessible to other segments for self diffusion, because of changes in molecular conformation and orientation, and so a correction factor (γ) is introduced such that the free volume change produced by strain ($\Delta V_{f,\text{strain}}$) is:

$$\Delta V_{f,\text{strain}} = \gamma \Delta V_{\text{strain}} = \gamma \epsilon (1-2\mu) \quad (4)$$

The free volume change produced by strain may be equated with that produced by an increase in temperature:

$$(\gamma \Delta V_{\text{strain}})_0^{\epsilon} = (\beta \Delta V_E)_T^{T^*} \quad (5)$$

where T^* is now a fictive sample temperature, ie the temperature at which an unstrained sample has an equivalent free volume. Yielding will occur when T^* exceeds T_g , ie when long range motion is possible.

$$(\gamma \Delta V_{\text{strain}})_0^{\epsilon_y} > (\beta \Delta V_E)_T^{T_g} \quad (6)$$

where ϵ_y is the yield strain.

We recognise that many more refined treatments of the free volume concept exist, and that the whole free volume approach to molecular mobility has its critics, but the chosen method has the advantage of conceptual simplicity, the ability to be quantified, and leads to verifiable predictions of the requirements for a ductile mode of failure. As a first approximation, the two constants of proportionality, β and γ , may be equated because factors responsible for an increase in occupied volume with temperature (making $\beta < 1$) will also produce an increase in occupied volume when the sample is strained (making $\gamma < 1$). Equations (5) and (6) therefore simplify to:

$$(\Delta V_{\text{strain}})_0^{\epsilon} = (\Delta V_E)_T^{T^*} \quad (7)$$

Ductile failure implies that yielding occurs at a strain lower than the brittle failure strain, ie

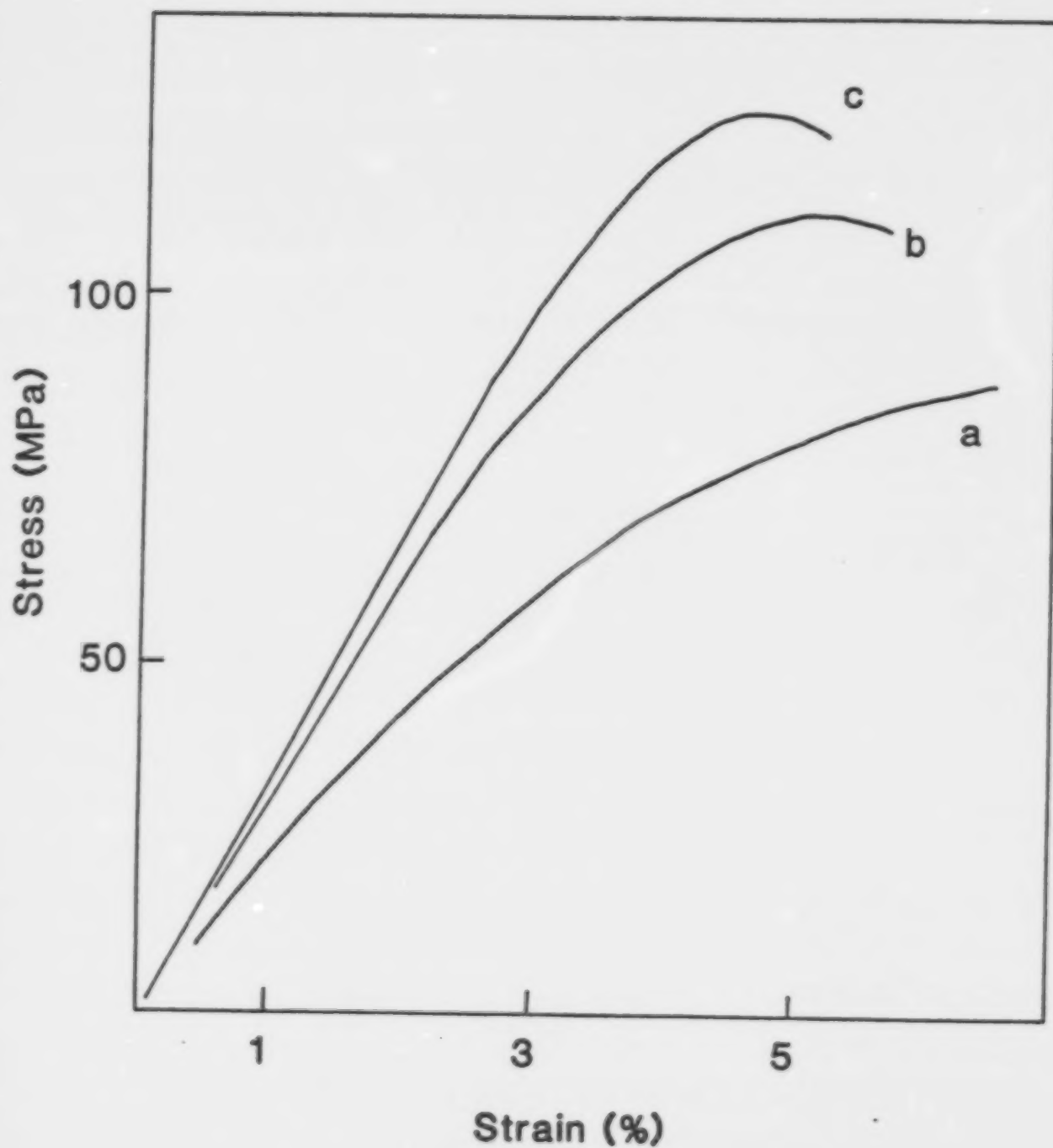


Figure 2 Tensile stress vs. strain at 25°C and 23 min⁻¹.

- (a) control
- (b) + 20 phr EPPHAA
- (c) + 30 phr EPPHAA

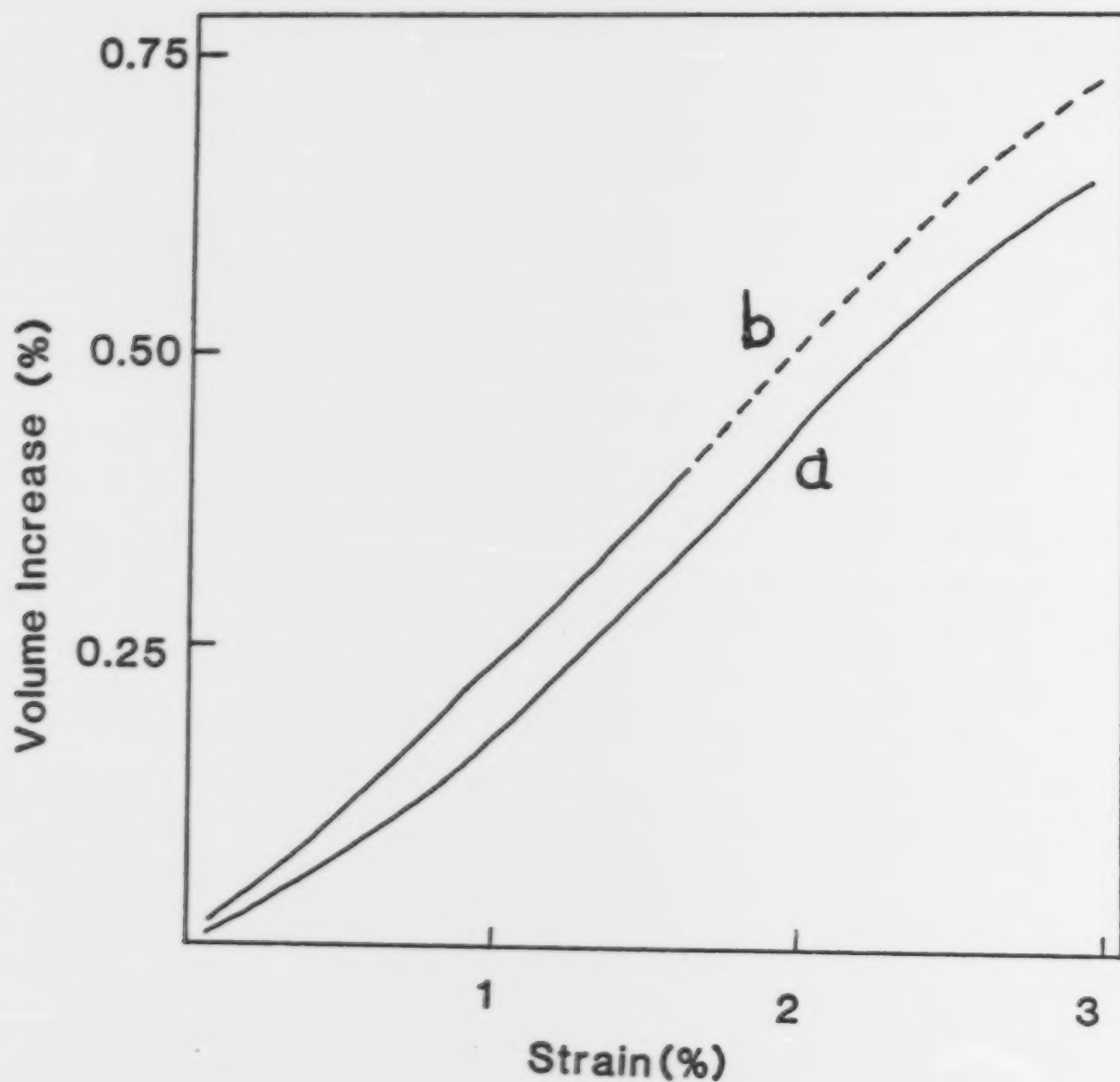


Figure 3 Volume expansion occurring during a tensile test at 25°C and 2%
min.
(a) control
(b) + 30 phr EPPHAA
— average of 4 specimens
---- data from one specimen which did not fail prematurely

$$(\Delta V_{\text{strain}})_0^{\epsilon_y} > (\Delta V_E)_T^g \quad (8)$$

This simple free volume interpretation of the occurrence of a ductile failure mode in the high modulus fortified plastic will be tested in the next section.

Application of Free Volume Model to Failure Characteristics

Figure 2 shows the tensile stress-strain curves for the epoxy/MDA system, with and without the additive EPPHAA. For specimens containing 20 and 30 phr EPPHAA, yielding and strain-softening occur at 4-5% tensile strain. The occurrence of this mode of tensile deformation has been shown previously to produce fracture surfaces which exhibit extensive localised plastic deformation(4,6). From an engineering viewpoint, such a material shows an attractive combination of stiffness, strength and ductile failure characteristics. Similar tensile curves are produced with the additive VCDHAA, as shown elsewhere(5,7).

The simplified free volume model described earlier requires the knowledge of the changes in sample dimensions during the tensile test. These data were provided by perpendicularly aligned glue-on strain gauges and are shown in Figure 3 for the epoxy/MDA system with and without the additive EPPHAA. The data are limited to relatively low strains so as to stay within the linear response range of the gauges and because the glue-on gauges caused premature failure of most specimens. It is immediately obvious from Figure 3 that the presence of the additive EPPHAA increased the extent of the strain-induced expansion in volume, ie decreased Poisson's ratio. As noted earlier, the volume change data were time depen-

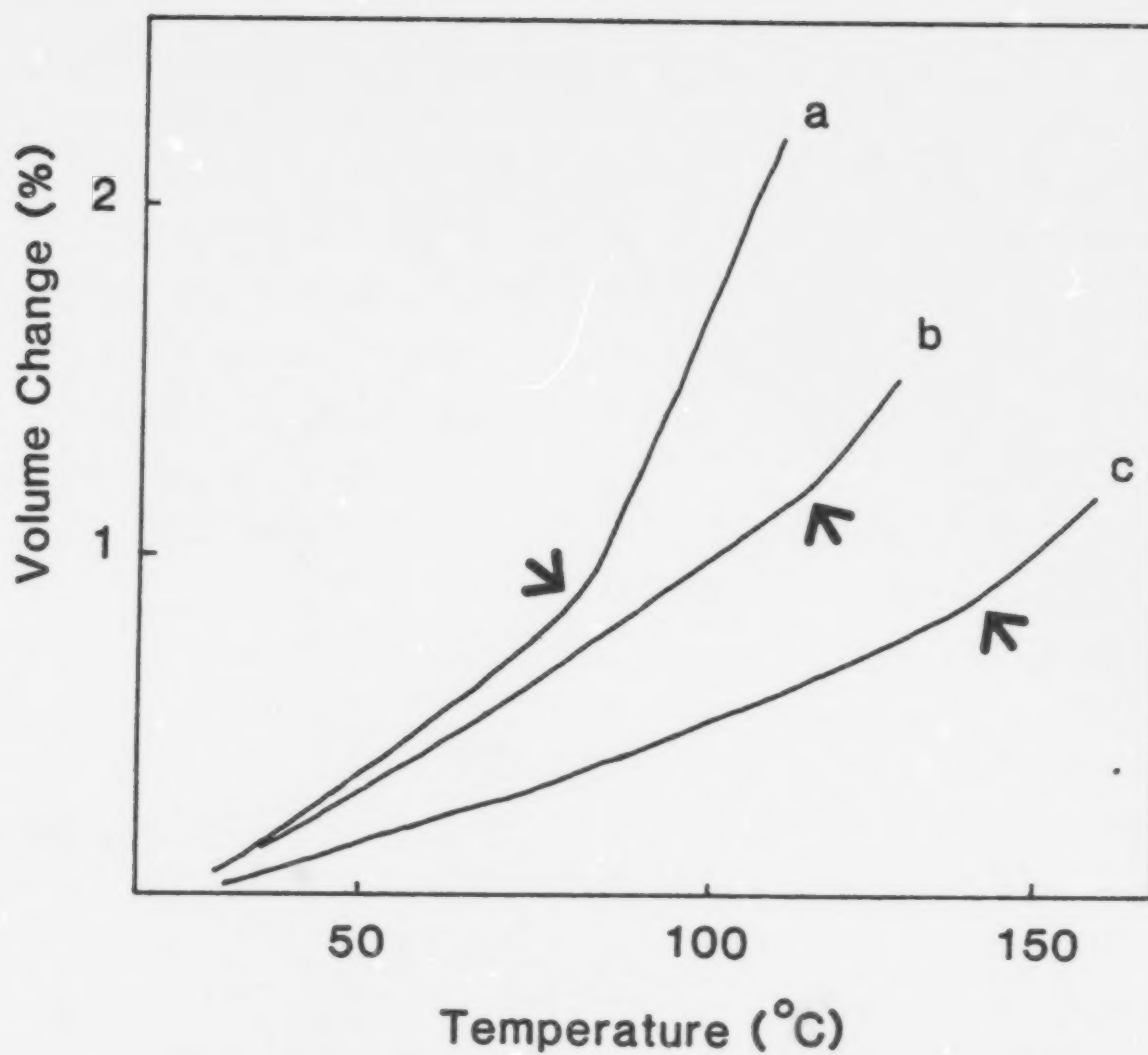


Figure 4 Thermal expansion by TMA, heating rate 10°C/min.

- (a) 30phr EPPHAA
- (b) 30 phr VCDHAA
- (c) 30 phr Fortifier Z

Arrows denote approximate Tg

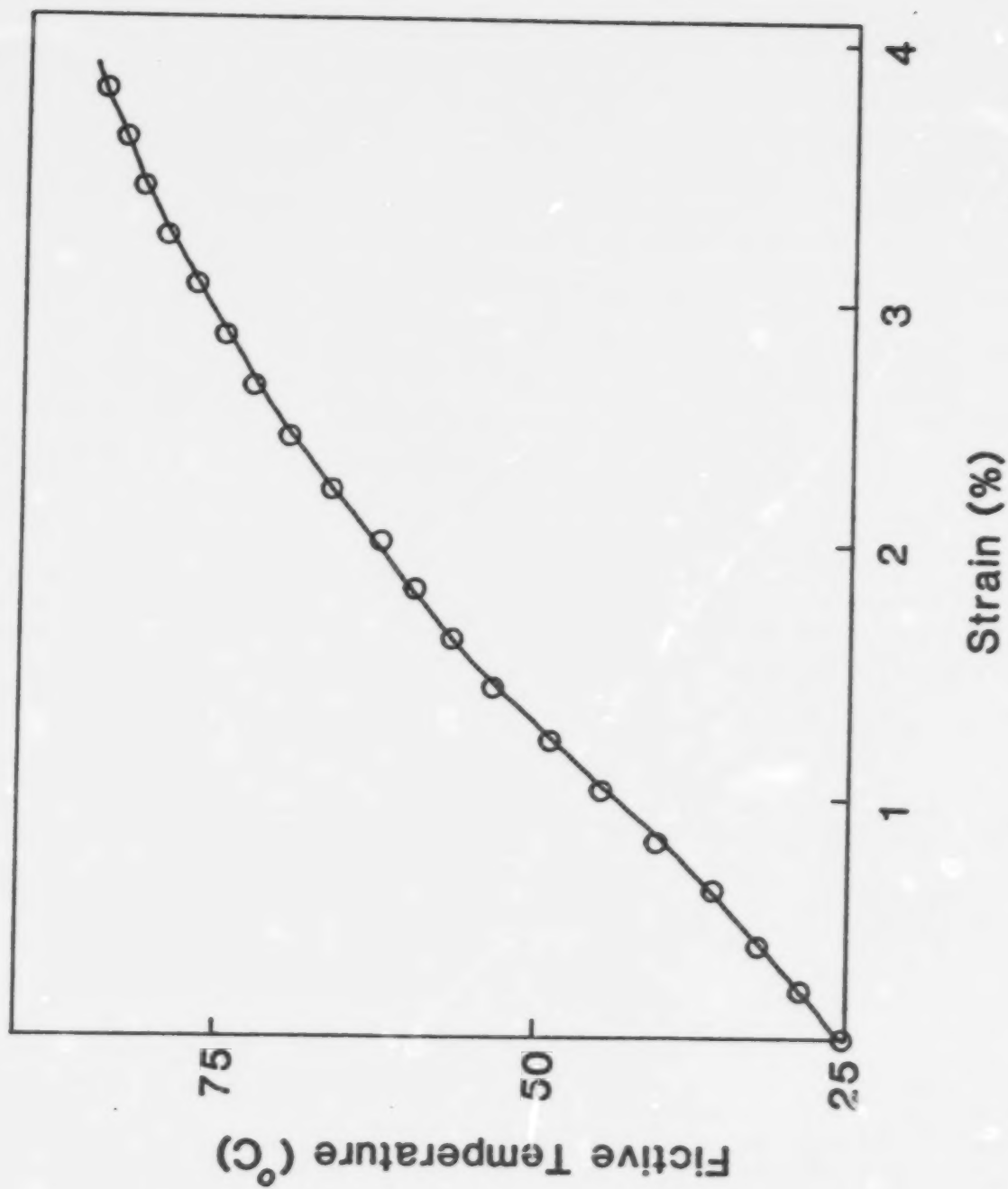


Figure 5 Fictive temperature vs. tensile strain for sample containing 30 phr EPPHAA.

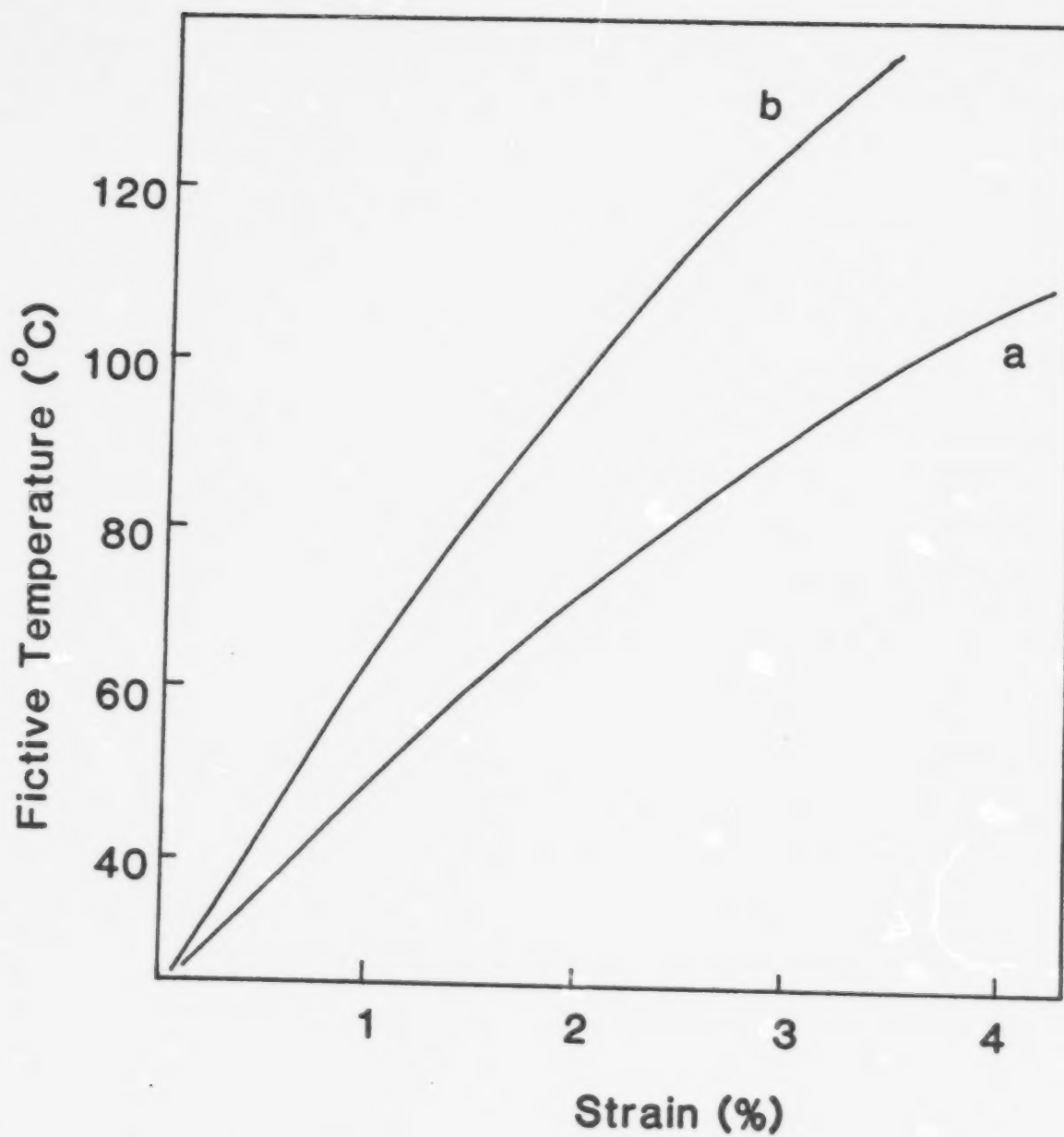


Figure 6 Fictive temperature vs. tensile strain.
(a) 30 phr VCD HAA
(b) 30 phr Fortifier Z

dent because of the viscoelastic nature of the polymer response. For example, if the direction of tensile strain was reversed during a tensile test, there was a marked difference in the two sets of volume vs. strain data.

Equation 7 requires thermal expansion data to be compared with the strain-induced volume change. Figure 4 shows the thermal expansion characteristics of the epoxy/MDA system with 30 phr EPPHAA, 30 phr VCDHAA, and 30 phr of a proprietary VCD-based fortifier designated Z. In each case the thermal expansion between room temperature and the T_g was about 1%. This should be compared to the additive-free epoxy/MDA system which expands > 2.3% on heating between room temperature and its T_g (ca 155°C).

The data for the strain-induced increase in volume (Fig 3) may be combined with the thermal expansion data (Fig 4), according to equation 7, to produce a relationship between the tensile strain and the fictive sample temperature. This is shown in Figure 5 for an EPPHAA-containing specimen, and in Figure 6 for VCDHAA and Fortifier Z-containing specimens. In each case it is apparent that tensile strains of 4-5% produce fictive temperatures close to the T_g of the unstrained material. The data in Figure 6 were calculated on the assumption that the strain-induced expansion characteristics were similar for all fortified systems (a reasonable assumption in view of their similar tensile properties). An exact identity between the limiting fictive temperature and the unstrained T_g is unlikely in view of the approximation involved in simplifying equation 5 to equation 7.

A similar calculation for the additive-free control shows that a tensile strain of 4% produces a fictive temperature of only about 75°C, ie appreciably below the T_g of the system (155°C). A strain of at least 8% would be necessary for ΔV_{strain} to be comparable to $(\Delta V_E)_{T_g}^T$, and brittle failure is likely to intervene before such a strain is reached.

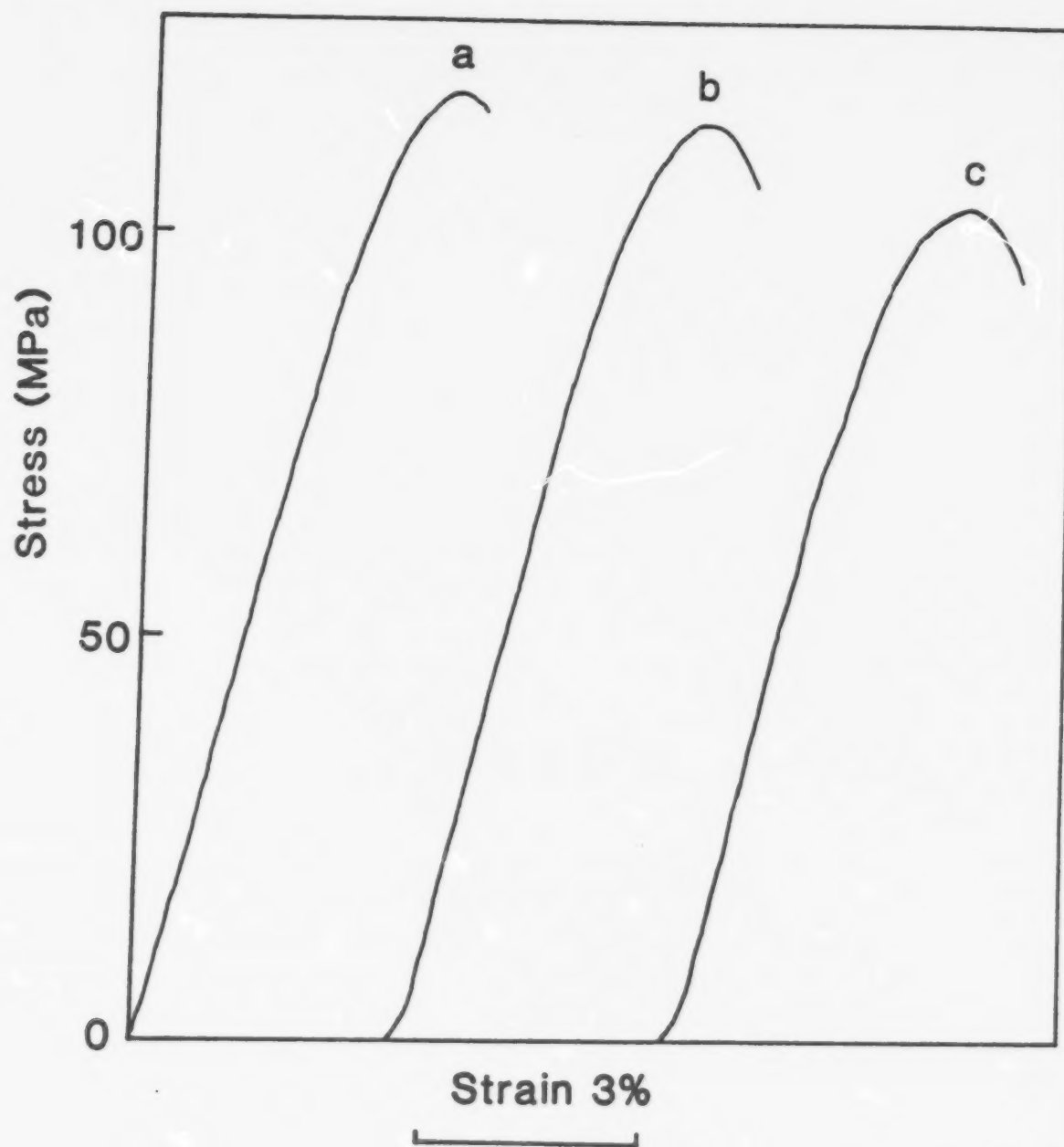


Figure 7 Tensile stress vs. strain at 25°C and 2% min⁻¹ for specimens containing 30 phr EPPHAA.
(a) cooled at 0.3°C/min
(b) cooled at 3°C/min
(c) cooled at >30°C/min

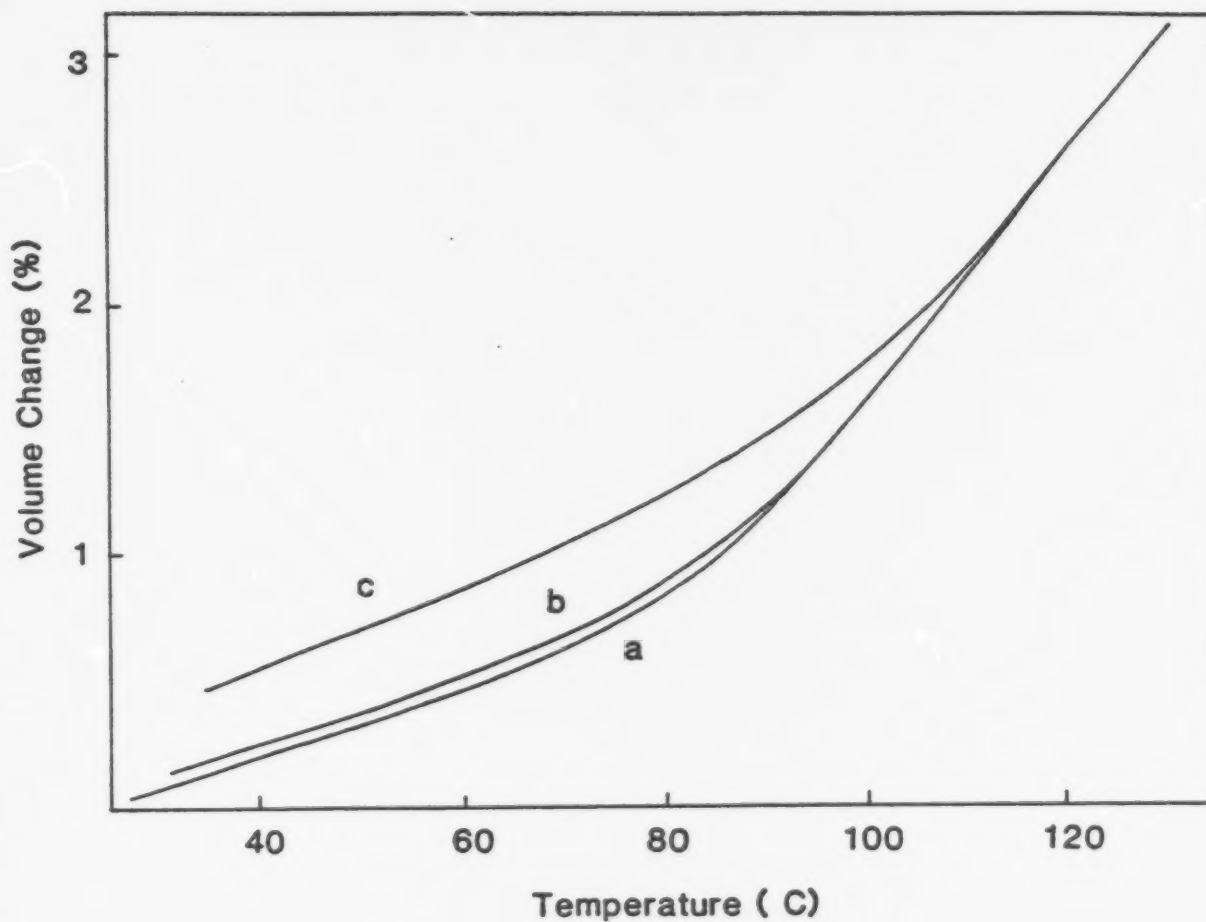


Figure 8 Thermal expansion characteristics of specimens containing 30 phr EPPHAA. Volumes normalised to identical volume:temperature curve at $T > T_g$. Heating rate $10^\circ\text{C}/\text{min}$.
(a) cooled at $0.3^\circ\text{C}/\text{min}$ through T_g
(b) cooled at $3^\circ\text{C}/\text{min}$ through T_g
(c) cooled at $>30^\circ\text{C}/\text{min}$ through T_g

If the occurrence of a ductile failure mode is related to free volume changes, then the mechanical properties would be expected to be influenced strongly by the thermal history, and in particular the rate with which the samples cooled through their T_g . A rapid rate of cooling freezes in excess free volume at the T_g because the rate of molecular reorganisation is insufficient to maintain equilibrium as the temperature falls. A rapidly-cooled sample may therefore be considered to have a higher fictive temperature T^* than the slow-cooled sample. The thermal expansion term in equation 7 is therefore reduced, and along with it the amount of strain-induced expansion required for yielding. Figure 7 shows that, as expected, an increase in cooling rate increases the extent to which the materials strain-soften before failure and also reduces slightly the strain at which yielding occurs. The occurrence of a ductile failure mode is also dependent on the size of the largest defect in the specimen (see Appendix) and so "ductility" (the occurrence of a negatively-sloping strain-curve before fracture) will have a statistical component. Table 1 shows clearly that an increase on cooling rate further increases the ductility of the EPPHAA-containing specimens. Conversely, prolonged annealing at close to the T_g will reduce the ductility, although it should be pointed out that the conventional fabrication procedure, involving a cooldown step of $<1^\circ\text{C}/\text{min}$ corresponds in itself to a relatively severe annealing history.

Figure 8 shows the thermal expansion data for EPPHAA-containing specimens which were cooled at various rates through the T_g . The free volume of this system shows a strong dependence on the rate of cooling, and inspection of Figure 8 shows that an increase in cooling rate from $0.3^\circ\text{C}/\text{min}$ to $>30^\circ\text{C}/\text{min}$ increases the fictive temperature of the glassy polymer by about 25°C . A similar cooling rate dependence was found for VCDHAA-containing

Table I
Effect of cooling rate on polymer properties

Sample	Cooling rate °C/min	Modulus GPa	Strength MPa	Ductility*
30phr EPPHAA	0.3	4.08±0.29	117±1.5	2/3
30phr EPPHAA	3		113±2.3	4/4
30phr EPPHAA	>30	3.78±0.12	103±2.4	5/5
Control	0.3	2.40±0.05	81±5	0/5
Control	3	2.38±0.12	82±3	0/5
Control	>30	2.35±0.08	80±2	0/6

* As defined in text

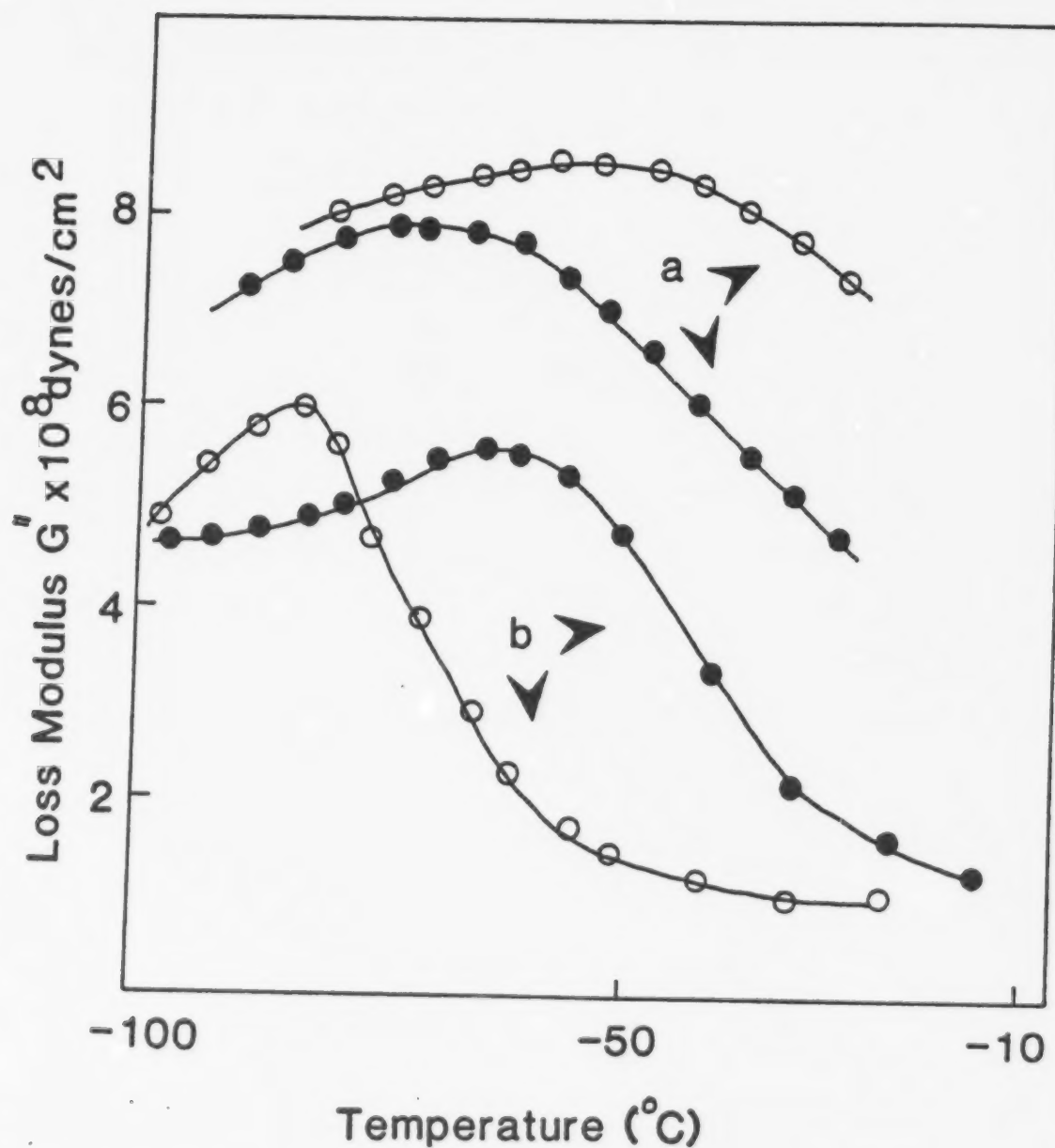


Figure 9 Dynamic mechanical properties at 0.1 and 10 Hz
 (a) ●● control 0.1 Hz
 ○○ control 10 Hz
 (b) ○○ 30 phr EPPHAA 0.1 Hz
 ●● 30 phr EPPHAA 10 Hz

specimens. Although an increase in the cooling rate also increased the free volume of the glassy control polymer, the magnitude of the change was less than half the value of the changes for the fortifier-containing specimens. This relative insensitivity of the control specimens to cooling rate is also reflected in the mechanical properties of the control system, which vary only slightly with the cooling rate (Table 1).

A complete description of the fortifier-containing systems in terms of a fictive temperature/free volume approach needs also to consider the effect of the rate of deformation. Figure 9 shows that just as the free volume of the EPPHAA-containing system is very sensitive to the cooling rate (Fig. 8), the mechanical response is also very sensitive to the rate of application of an oscillatory strain. As we reported previously(4), the effect of fortifier is to reduce the magnitude of the low temperature relaxations, as determined by dynamic mechanical analysis (DMA), and so cause a reduction in molecular mobility. Figure 9 shows that the characteristics of the low temperature relaxations (which will affect the room temperature mechanical properties) are strongly dependent on the rate of strain. Note that these data refer only to very small strains, and so the effect of strain-induced expansion, as seen in the tensile test, is insignificant. Although the response of the control specimens to oscillatory strain also varies with the strain rate, the magnitude of the variation is appreciably less than with the fortifier-containing specimens. The implication then is that the activation energy for the low temperature process is increased by the presence of the fortifier, consistent with the idea of strong specific interactions between the additive and the polymer(4).

Conclusions

Additives which increase the stiffness of crosslinked epoxy resins may also increase the ability of the plastic to yield before fracture, provided (a) they increase the coefficient of strain-induced expansion (ie decrease Poisson's ratio) and (b) they decrease the thermal expansion volume in the temperature range between the test temperature and the Tg. The data reported here give no direct evidence of the molecular basis for this phenomenon, although the observations are entirely consistent with a simple free volume interpretation, where strong intermolecular interactions between the additives and the polymers decrease segmental mobility. The effect of stress on these interactions could provide an explanation for the observed decrease in Poisson's ratio, but independent molecular evidence, eg spectroscopic studies under conditions of high stress, would be necessary to confirm this hypothesis.

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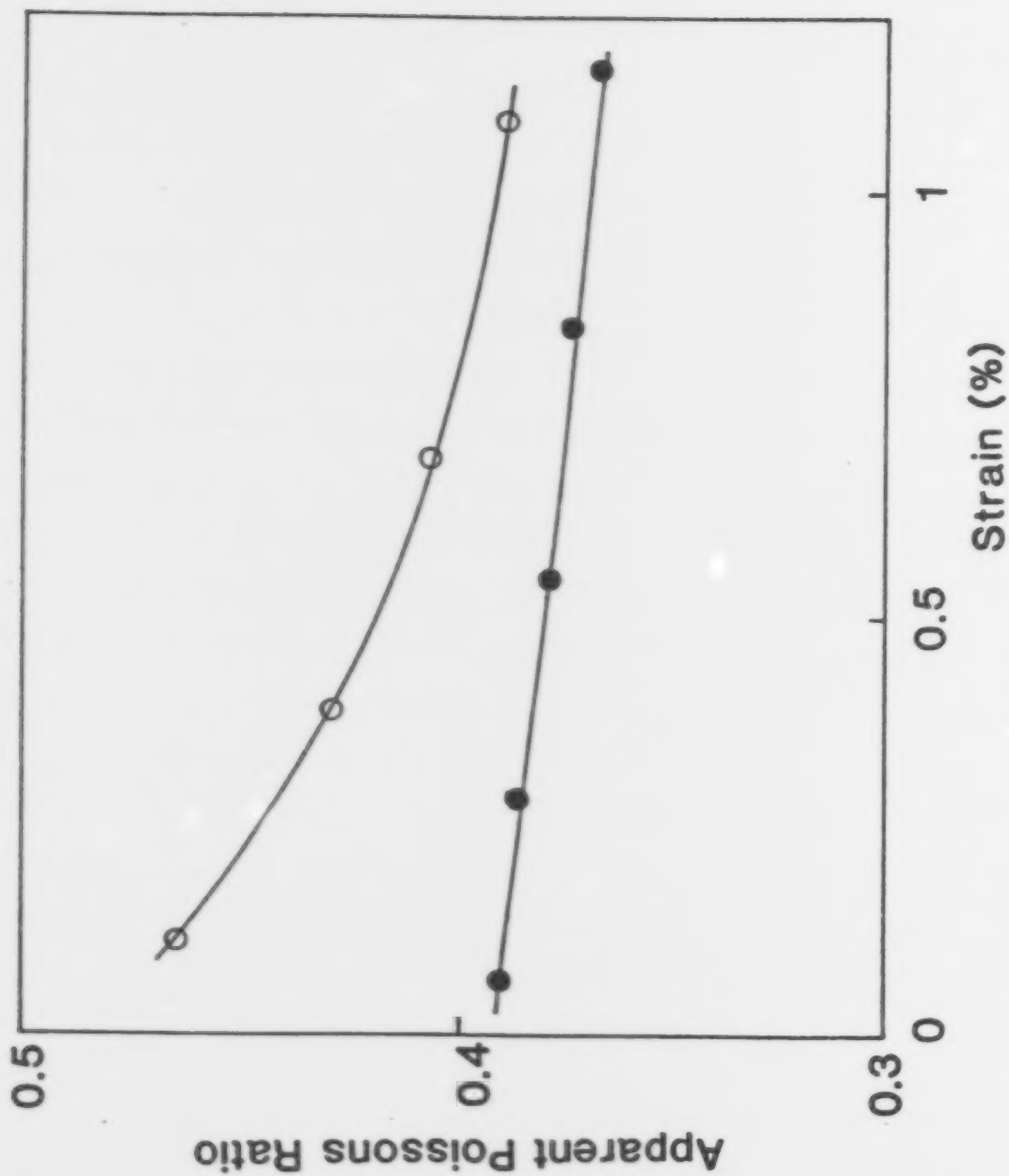


Figure 10 Apparent Poisson's ratio from perpendicular strain gauges.
○ control, ● 30 phr EPPHA

Appendix A Measurement of Poisson's Ratio

Although, as was pointed out earlier, Poisson's ratio is a time-dependent property because of the viscoelastic response of the plastic, the value of Poisson's ratio is meaningful as long as the method of measurement is adequately defined.

Figure 10 shows the apparent Poisson's ratio calculated from the perpendicularly aligned strain gauges on the tensile test dogbone. Irrespective of the "true" value for Poisson's ratio, it is clear that the numerical value under identical conditions is appreciably reduced by the presence of 30phr of the additive EPPHAA.

An apparent Poisson's ratio may also be calculated from a comparison of the tensile modulus (E, from the tensile test) and the shear modulus (G from DMA) using the relation.

$$E=2G(1+\mu) \quad \text{where } \mu=\text{Poisson's ratio}$$

Using DMA data obtained at 0.1 rads/sec, the Poisson's ratio was again lower in the EPPHAA-containing specimen than in the control (0.28 compared to 0.32).

Appendix B Effect of Defects (Stress Concentrators)

It should be recognized that not all samples containing fortifiers will fail in a ductile fashion. If a sample contains a sufficiently large (or sharp) defect, premature failure will occur in a brittle fashion.

At an overall tensile stress $\bar{\sigma}$, the stress σ at the tip of a flaw of length l and tip radius r is given by :

$$\sigma/\bar{\sigma} = K = 1 + 2(l/r)^{1/2}$$

At large values of K , the local stress at the crack tip greatly exceeds the stress experienced by the material displaced from the tip, and the yielding will therefore be restricted to a thin band restrained between two relatively rigid regions of glassy polymer. The effect of the restraint is to further amplify the stress concentration at the defect and failure will occur in a very narrow region (thin-band softening). At lower values of K , the stress is not so localized at the tip and yielding can occur over a larger volume of the specimen. The more generalised yielding also reduces the additional stress concentration due to the restraint of the surrounding glassy polymer, and so a transition occurs from thin-band softening (which will appear as a brittle mode of failure, possibly accompanied by crazing) to a general plastic yielding (which will appear as a ductile mode of failure).



Rheological Properties of LLDPE/PP Blends

Part 2: Solid State Behaviour

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ABSTRACT

This 2nd paper of a series continues the examination of the tensile properties of two series of LLDPE/PP blends. The blends were prepared using a twin-screw extruder and cover the whole concentration range. An Instron Universal Tensile Tester was used to measure the tensile properties of the blends between 10 and 70 °C and the temperature and composition dependences of the modulus were examined. A comparison is established between the solid state and melt properties to underline the behaviour in the PP rich region. Results of dynamic mechanical experiments and differential scanning calorimetry on the same materials are also given and the mechanical behaviour is discussed in terms of the variation of the system's crystallinity.

INTRODUCTION

Because of their relatively low cost and versatile properties, polyolefins are the principal commodity thermoplastics. Consequently, their blends have attracted much interest (1-15). Processability and improvement of the impact properties of polypropylene, PP, are often the reasons for preparation of these blends. Ductile materials such as polyethylene, PE, or elastomers can be used for the latter purpose. Morphological studies have clearly shown the two-phase structure of these blends (8,9,14,15). This structure is expected to induce a deterioration in some mechanical properties. For semi-crystalline polymers, however, the presence of one phase might bring about changes in the crystallization process of the other, resulting in a profound influence on the mechanical behaviour of the system (7-9,11).

These observations may explain the apparent conflicts in the literature on the properties of PE/PP blends. Quite different behaviour has been reported for apparently similar systems. A linear relationship between the modulus and the composition was observed for blends of PP with high density polyethylene, HDPE, by some authors (1,6), while others reported a large positive deviation (2,4). Although encouraging results are often obtained for the low

TABLE 1
PROPERTIES OF MATERIALS

Material	PP	LLDPE-1	LLDPE-2
Manufacturer	Hercules	Esso	Dow
Designation	6701	LPX-24	Dowlex 2517
Density at 23°C (kg/m ³)	900	951	917
Melt index (dg/min)	0.8	0.3	25
η_0 at 190°C (kPa·s)	13	25800	1.3
Poisson ratio, ν	0.43	0.48	0.48

strain properties such as the modulus or the tensile-strength, a drastic deterioration in the ultimate properties, such as the strain at break, is often the price one has to pay (1,5,8). The Deanin et al. results stressed the considerable influence of the molecular weights of the components on the solid state properties (4,6). The same works also showed negative deviations for the yield stress, the strain at yield and the ultimate strain, implying that the effect of the two-phase structure is already felt at yield.

The present work examines the rheological behaviour of LLDPE/PP blends both in solid and molten states. Two different blends were studied in order to take into account the effect of the molecular weight of the components. This paper reports on the solid state properties of these blends.

EXPERIMENTAL

MATERIALS. Isotactic commercial PP was blended with two linear low density polyethylenes, LLDPE. Properties of the resins are given in Table 1. Two systems were prepared by blending each of the PE resins with PP. The polymers were selected in order to obtain pairs of components with different viscosity ratios. As the zero-shear viscosity values in Table 1 indicate, in one case the polyethylene is the more viscous component (LLDPE-1) while the situation is reversed for the other blend (LLDPE-2/PP). Seven compositions of 0, 5, 25, 50, 75, 95 and 100% were prepared on a Werner Pfl-

derer twin-screw extruder at 245 °C. The granulated materials were injection molded using a single-gated mold to produce ASTM type 1 dumbbell specimens for mechanical testing. Prior to testing, the specimens were annealed at 70 °C for 72 hours.

TESTING. The tensile properties were measured using an Instron Tensile Tester, model 1123, at 23 °C with a cross-head speed of 50 mm/min. The modulus was taken as the slope of the initial straight line portion of the stress-strain curve. The strain, ϵ , was computed as the elongation divided by the initial length of the sample.

The dynamic mechanical properties were measured with the Dynamic Mechanical Thermal Analyser, DMTA, from Polymer Laboratories, in the single cantilever bending mode. The dynamic moduli, E' and E'' , were measured between -150 and 150 °C at a constant frequency of 1 Hz and a heating rate of 2 °C/min.

The differential scanning calorimetry, DSC, was performed with a Perkin Elmer calorimeter, model DSC-7. From 3 to 5 mg of the granulated materials were first heated from 25 to 250 °C at a rate of 10 °/min. After cooling at 40 °/min, the melting endotherms were recorded at a rate of 10 °/min.

The morphology of the blends was examined with a Jeol scanning electron microscope, SEM, model JSM-35CF. The surfaces were prepared by fracture under liquid nitrogen of injection molded specimens.

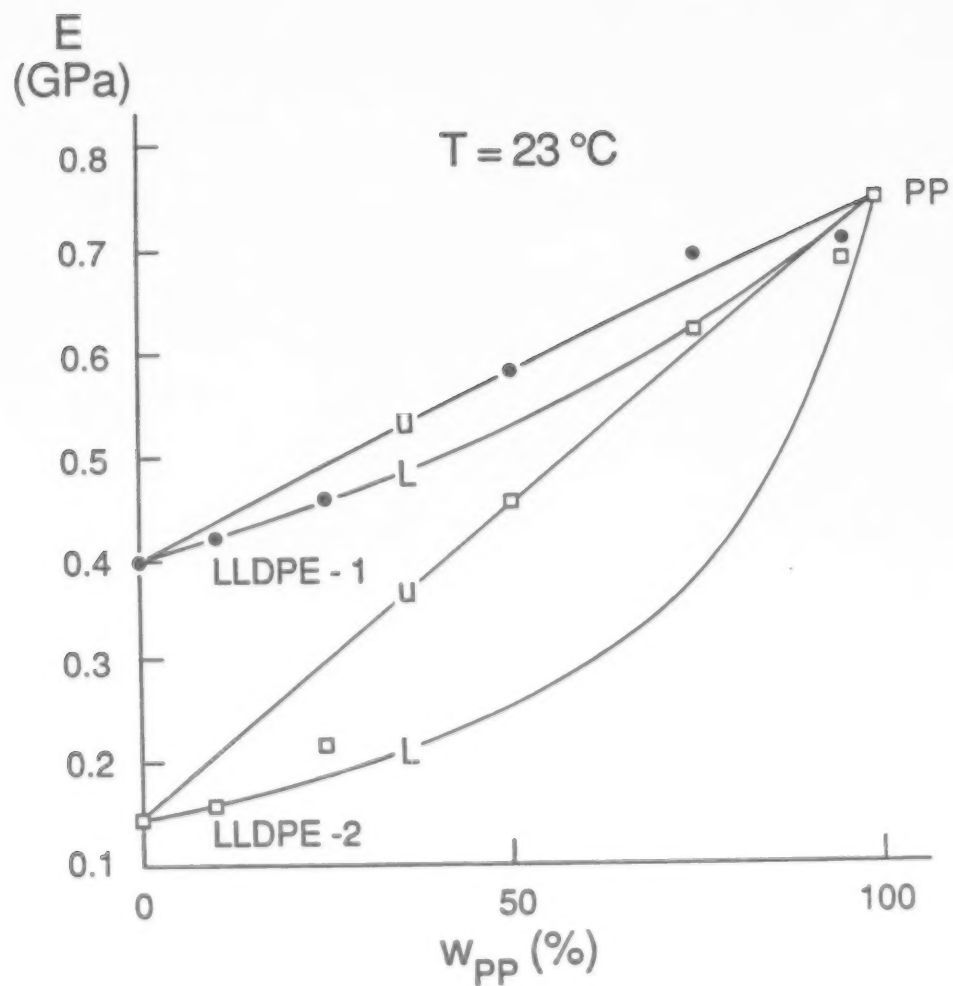


Fig. 1 Young's modulus, E , at ambient temperature for systems 1 and 2 as a function of composition.

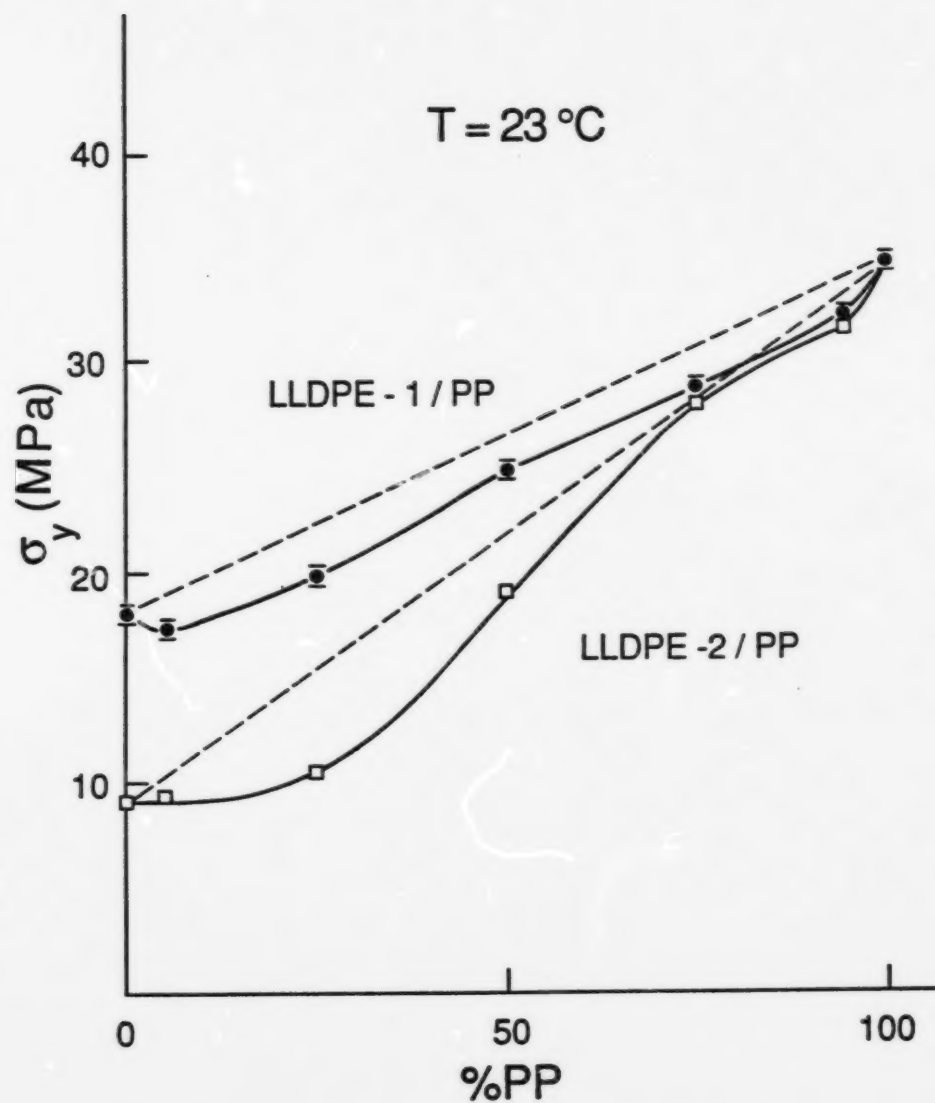


Fig. 2 Yield stress, σ_y , for systems 1 and 2 as a function of composition.

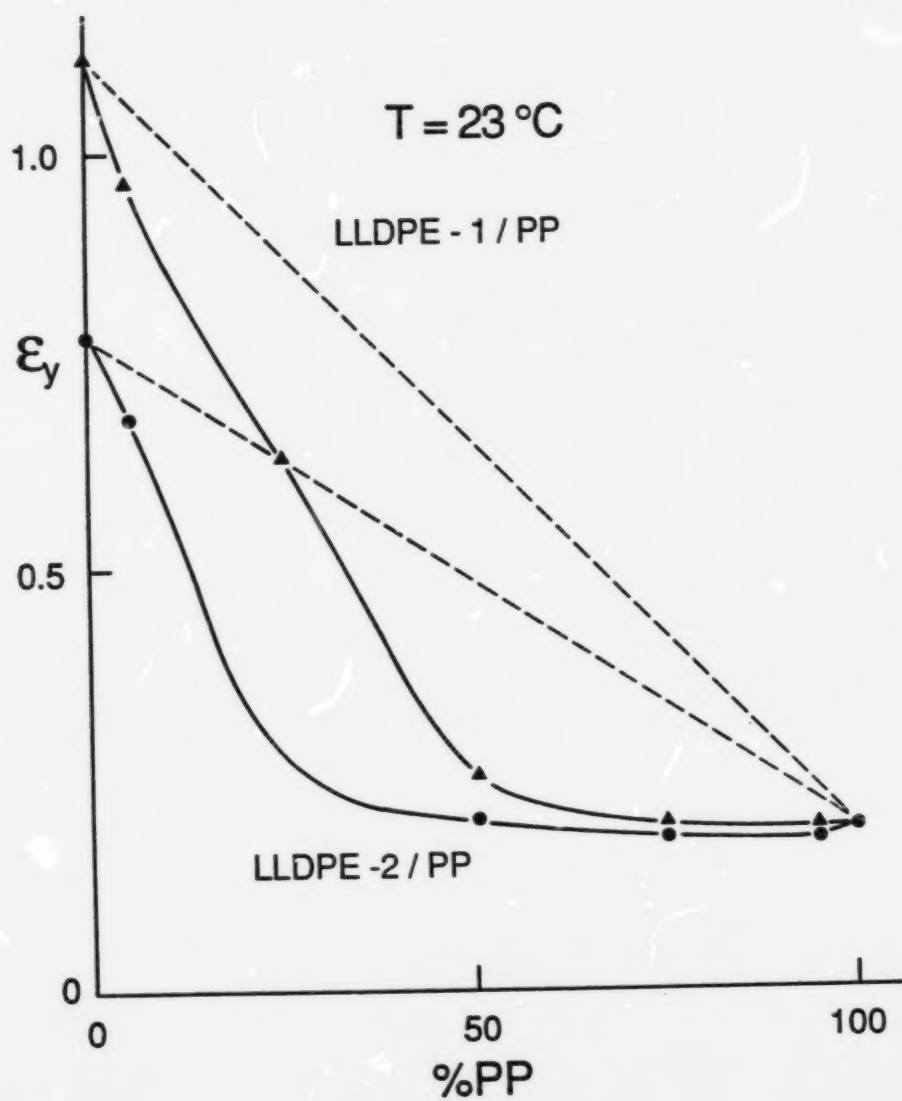


Fig. 3 Strain at yield, ϵ_y , for systems 1 and 2 as a function of composition.

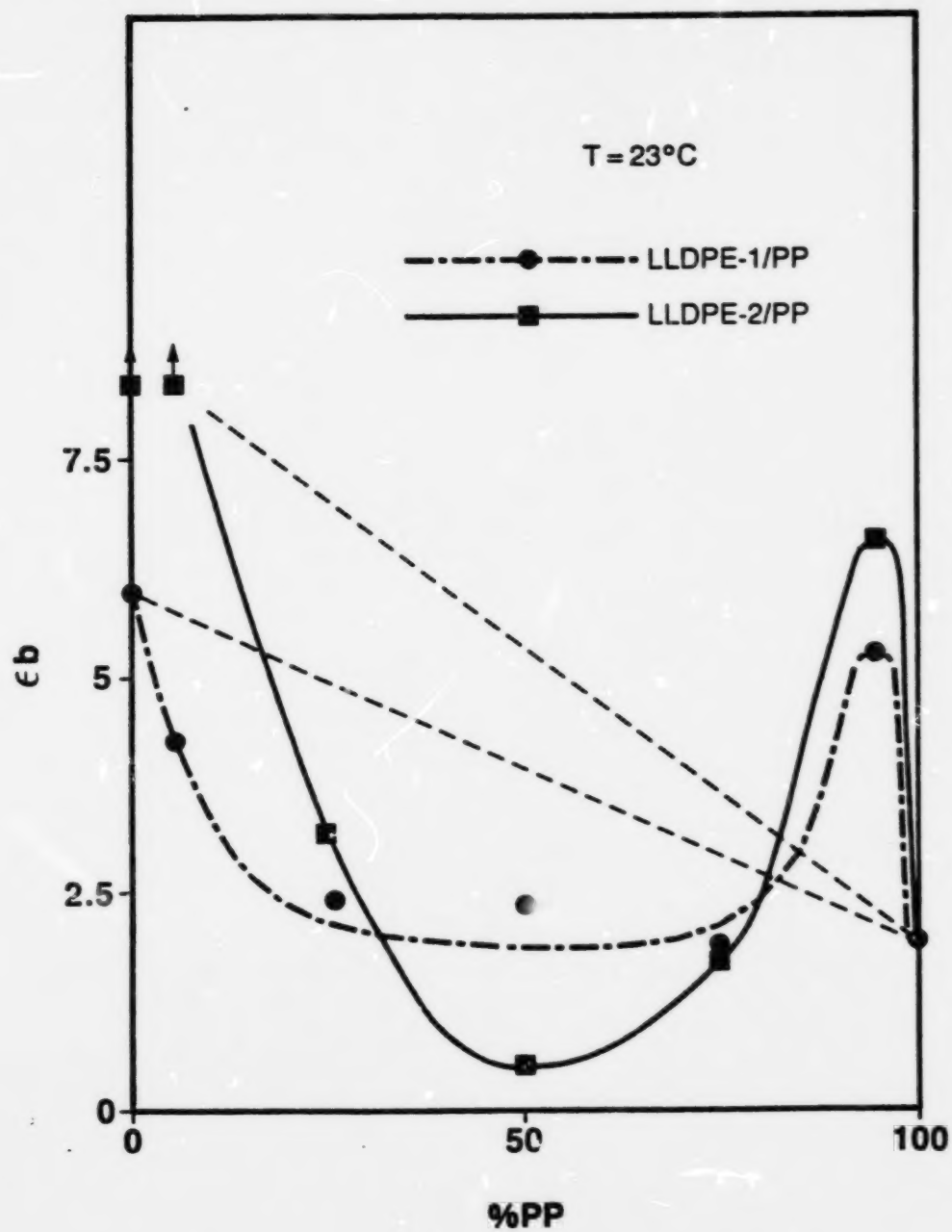


Fig. 4 Strain at break, ϵ_b , for systems 1 and 2 as a function of composition.

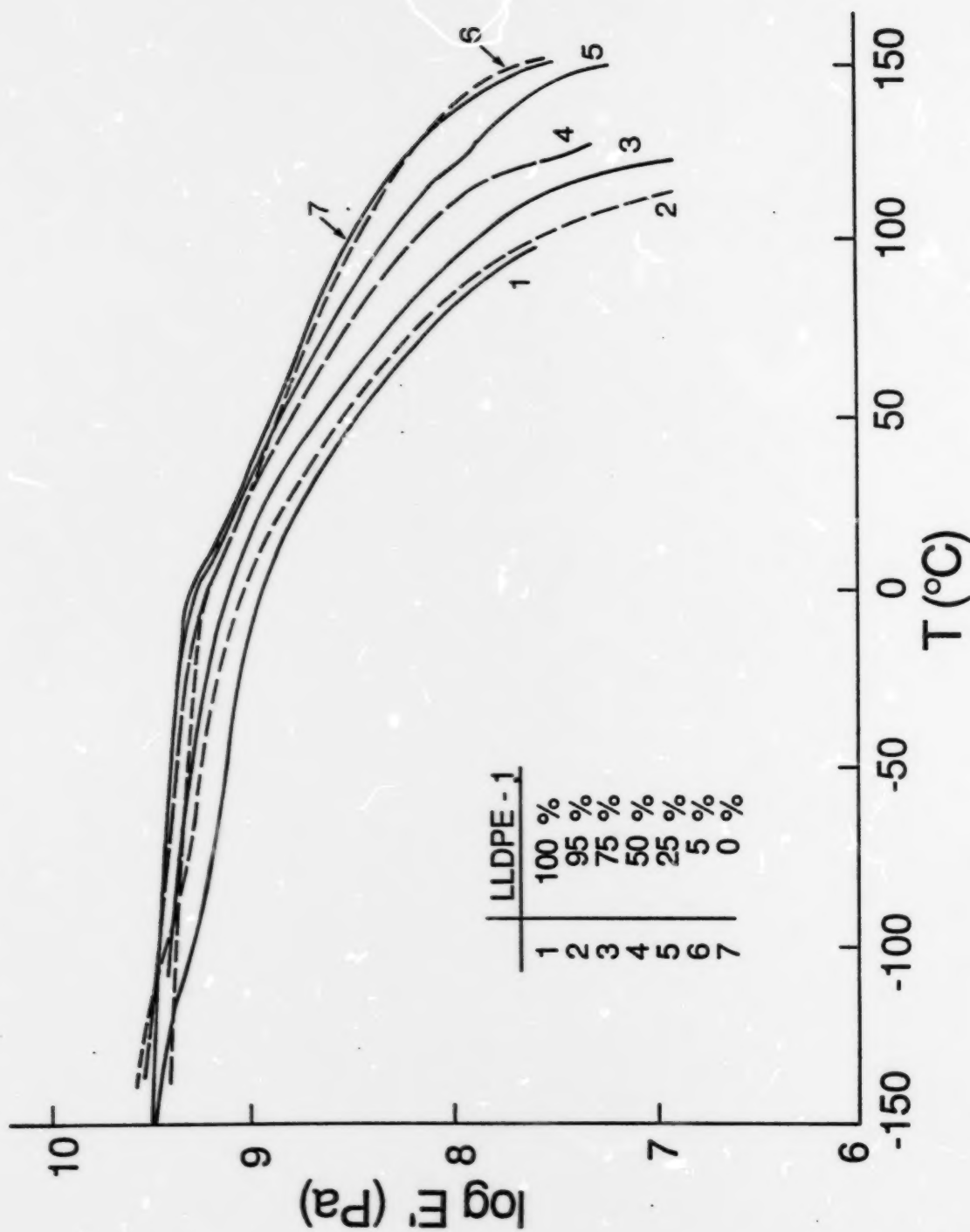


Fig. 5 Storage modulus, E' , as a function of temperature for system 1.

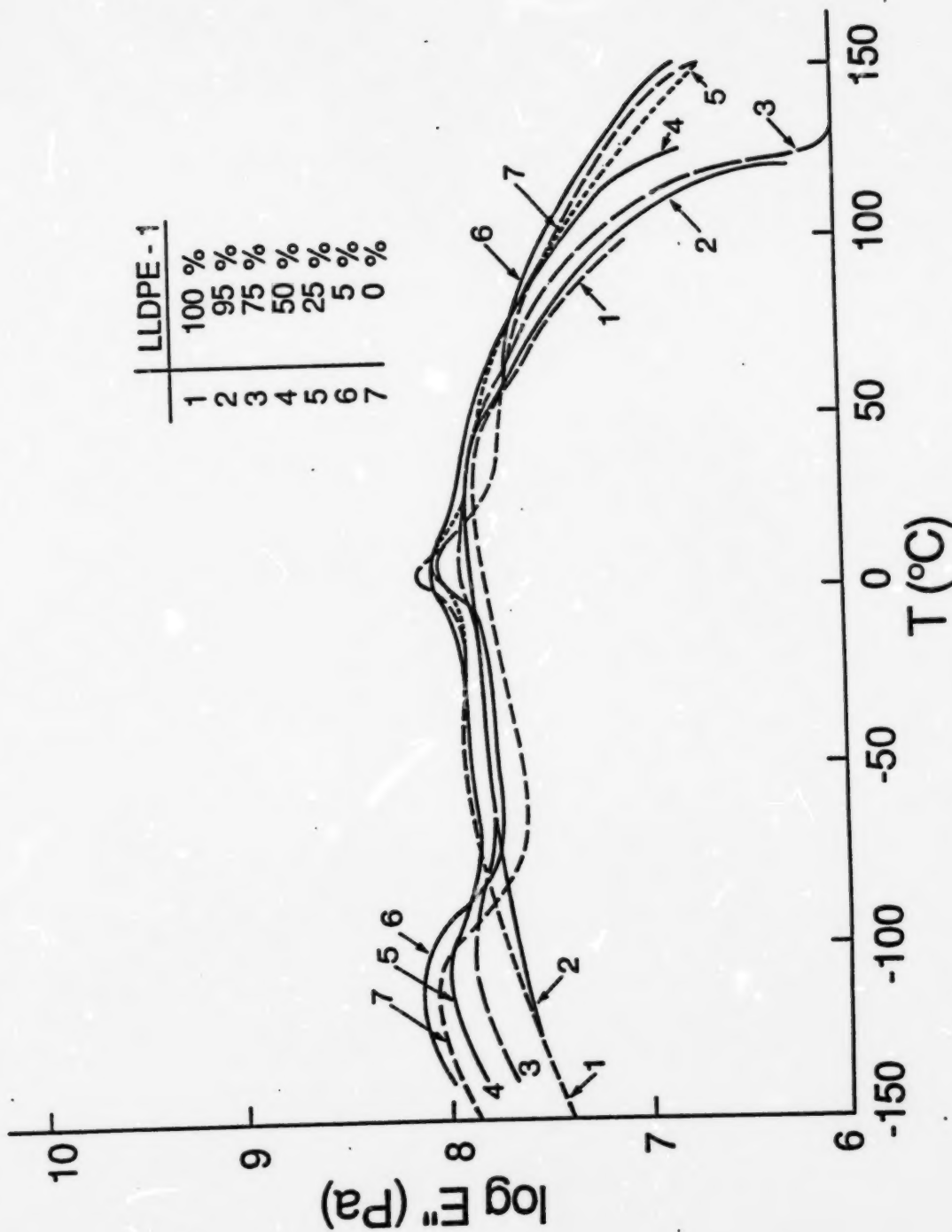


Fig. 6 Loss modulus, E'' , as a function of temperature for system 1.

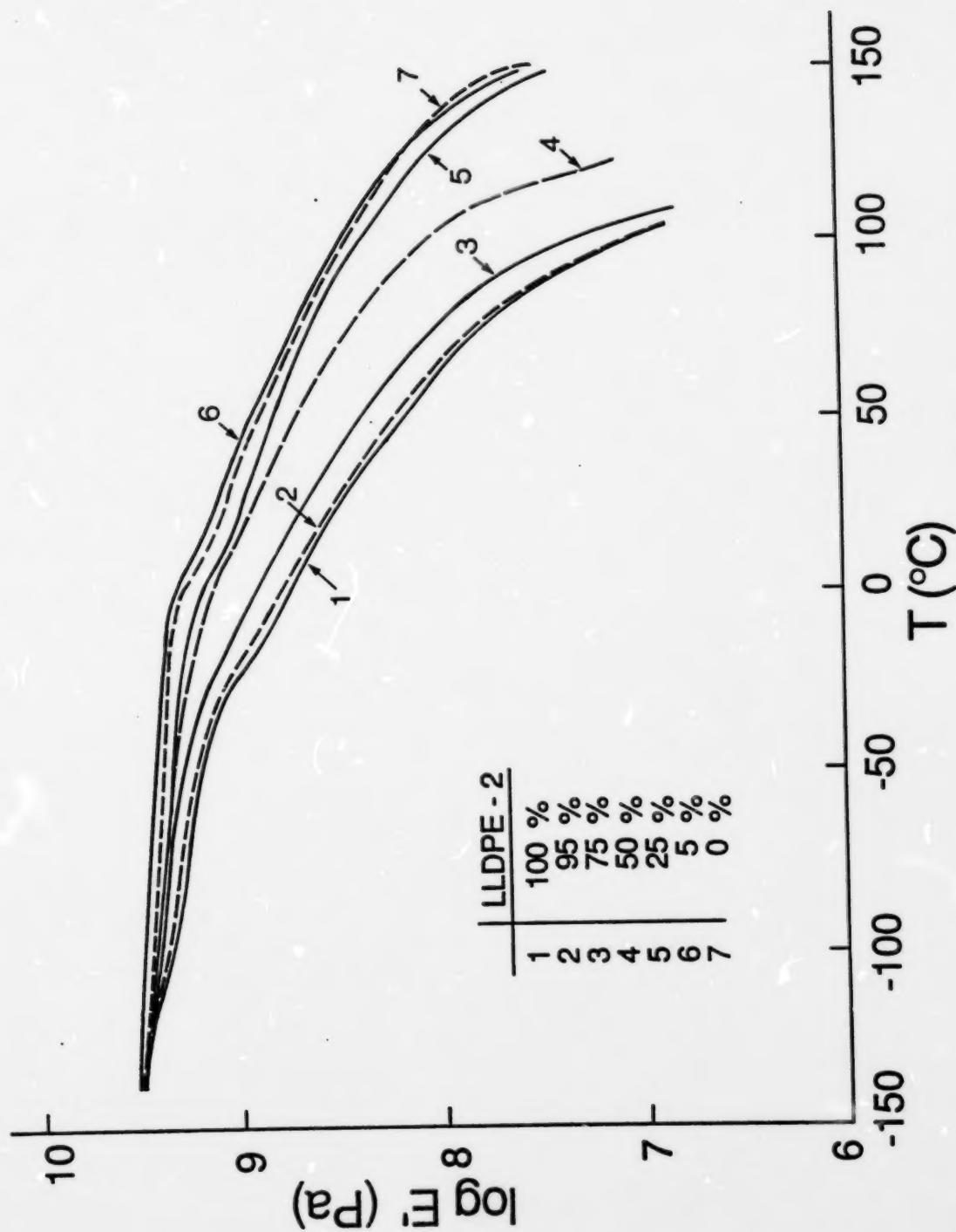


Fig. 7 Storage modulus, E' , as a function of temperature for system 2.

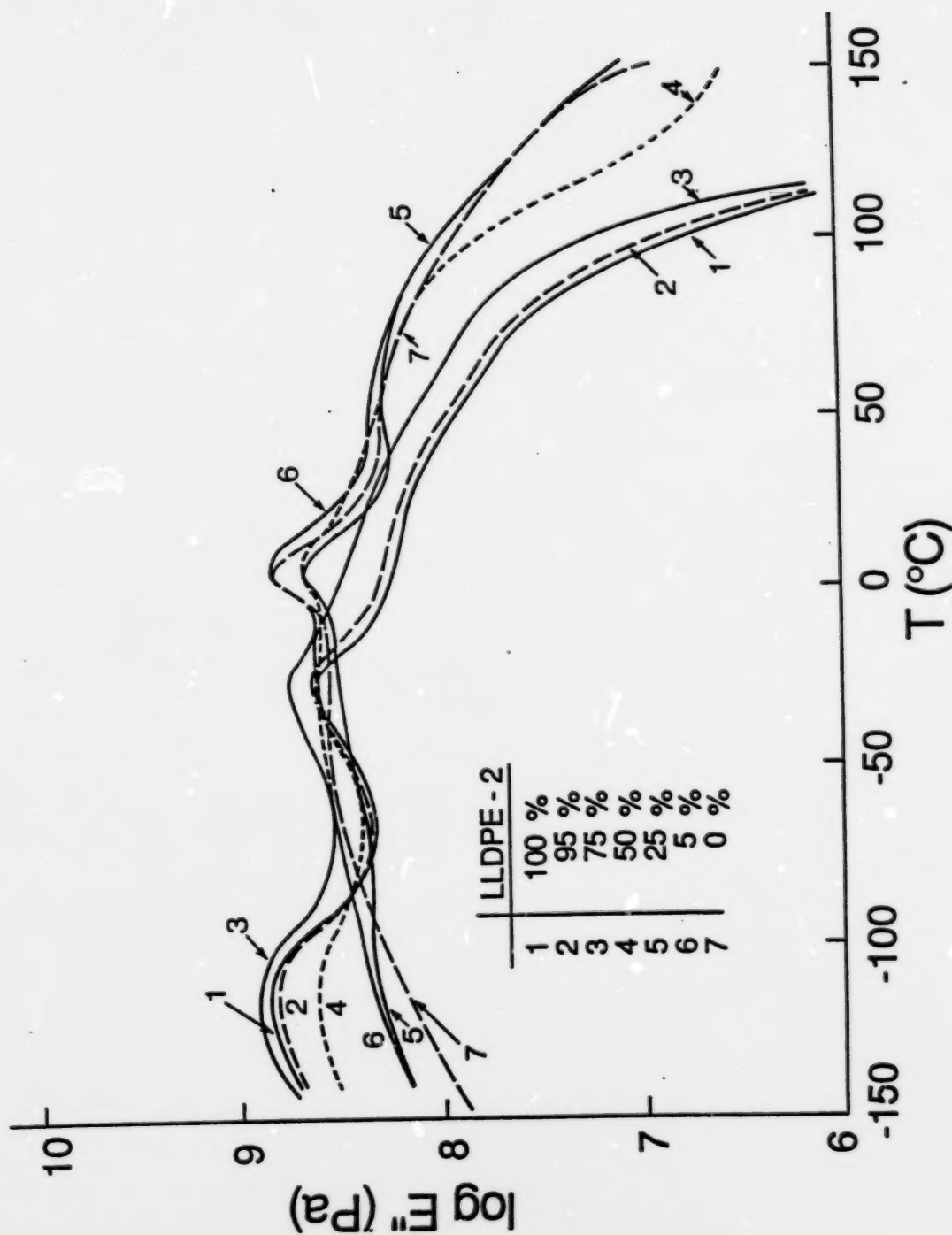


Fig. 8 Loss modulus, E'' , as a function of temperature for system 2.

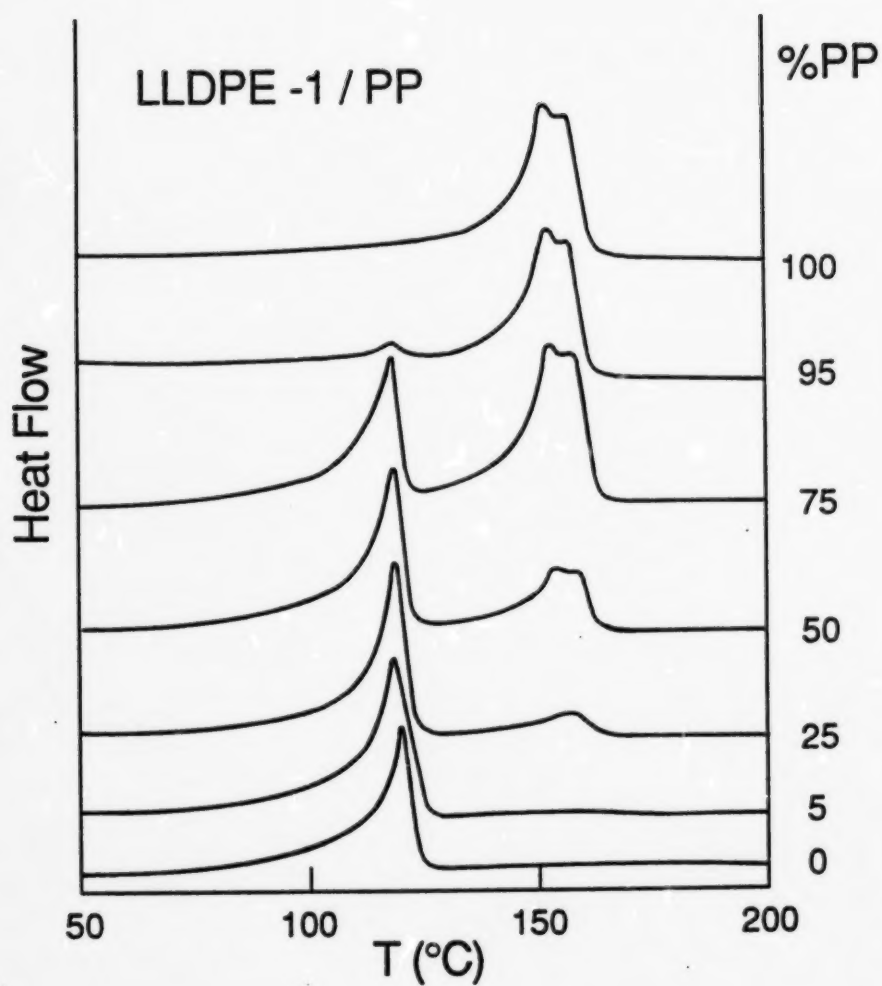


Fig. 9 Heat flow as a function of temperature for system 1.

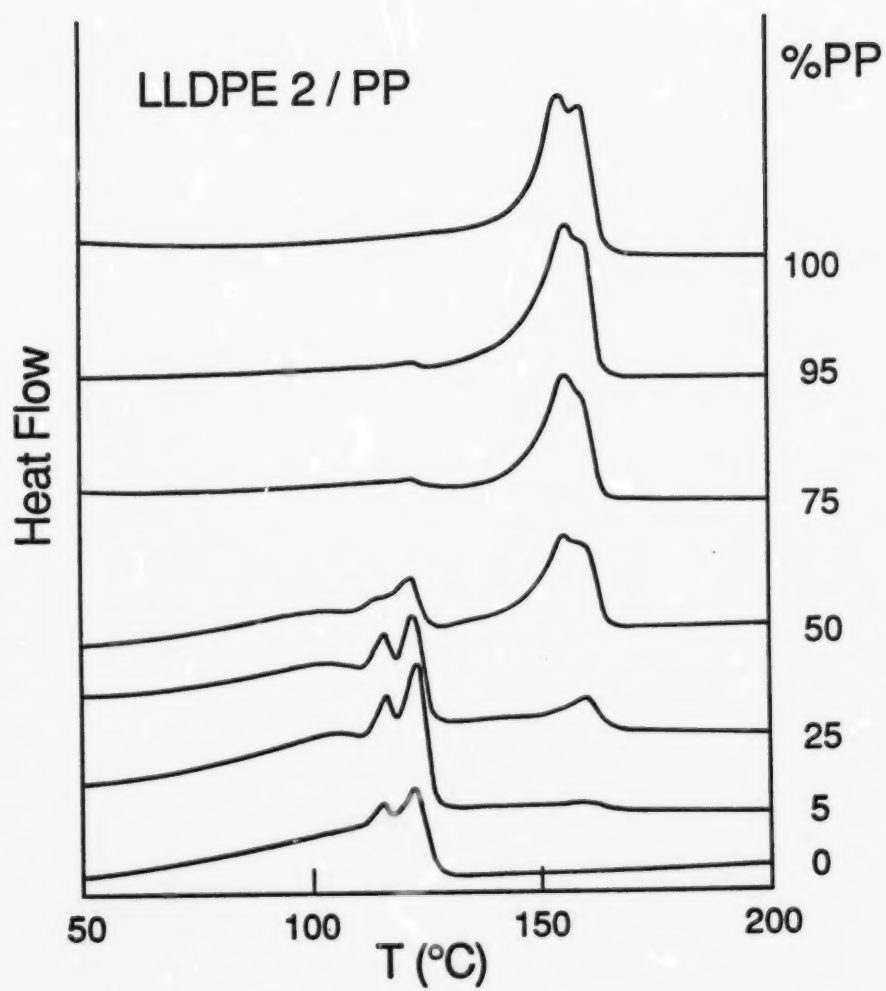


Fig. 10 Heat flow as a function of temperature for system 2.

RESULTS

The mechanical behaviour of both systems is summarized in Figs. 1 to 4 showing respectively the composition dependences of the Young's modulus, E , the yield stress, σ_y , the strain at yield, ϵ_y , and the strain at break, ϵ_b . In all graphs the broken lines represent a linear additivity rule while the curves follow the experimental data. For all properties, the behaviour is similar for both systems despite the difference in molecular weights for the LLDPEs. For the Young's modulus a negative deviation is observed for the LLDPE rich region while a positive deviation can be seen for PP contents of 50% and higher. Both the stress and strain at yield show negative deviations for all blend compositions, as seen in Figs. 2 and 3. In Fig. 4 a strong negative deviation is seen for the strain at break except for a narrow concentration region around 5% LLDPE; in this range ϵ_b was increased to over 600%. The PP matrix completely lost its brittle character upon addition of 5% of LLDPE. For compositions containing more than 10-15% of LLDPE the ultimate strain decreased dramatically.

The results of dynamic mechanical experiments are shown in Figs. 5 to 8; the storage, E' , and loss, E'' , dynamic moduli for system 1 appear in Figs. 5 and 6 while those for system 2 are in Figs. 7 and 8.

The DSC thermograms (second heating) for systems 1 and 2 are presented respectively in Figs. 9 and 10. For the

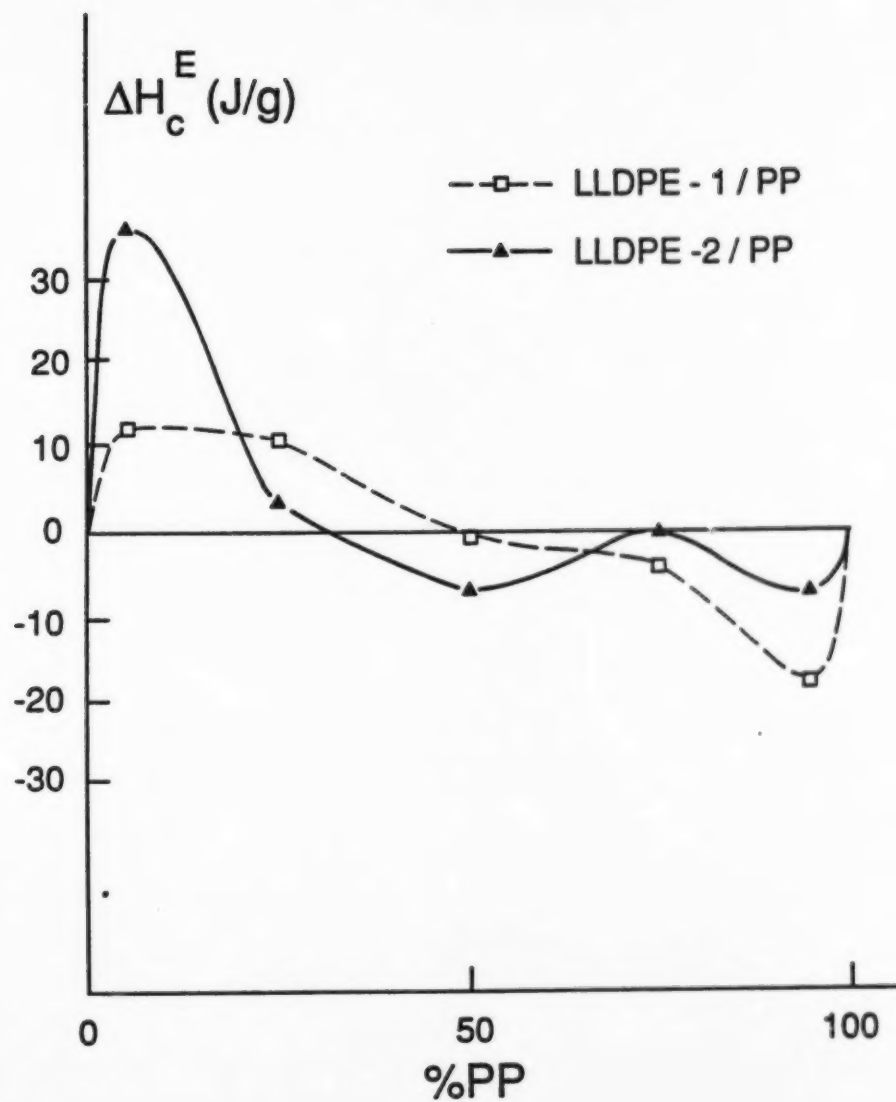


Fig. 11 Excess heat of crystallization, ΔH_c^E , as a function of composition for systems 1 and 2.

sake of clarity, the curves have been displaced vertically.

DISCUSSION

Three elements dictate the mechanical properties of polymer blends: total crystallinity, morphology and the interfacial properties. The first can be estimated from the DSC experiments, the second from detailed morphological studies while the last may be deduced from the mathematical analysis of mechanical properties assuming a realistic model of the system.

To examine the effect of blending on the crystallinity of the system, the excess enthalpy of crystallization has been calculated according to:

$$\Delta H_C^E \equiv \Delta H_C - \sum w_i \Delta H_{C,i} \quad (1)$$

where w_i is the weight fraction of component $i = 1, 2$, ΔH_C and $\Delta H_{C,i}$ are measured heats of crystallization for the blends and pure resins respectively. The ΔH_C^E vs composition plot is shown in Fig. 11 for both systems. The large positive value for the composition containing 95% of LLDPE-2 indicates increased crystallinity of the blend. In other words, the addition of a small quantity of PP to LLDPE enhances crystallization; the effect is more pronounced for the lower molecular weight LLDPE-2. At the other end of the composition scale, the negative values for ΔH_C^E indicate LLDPE lowers the crystallinity of the PP matrix. For this purpose the more viscous LLDPE-1 seems more effective.

As seen in Figs. 9 and 10, LLDPE-2 and PP showed

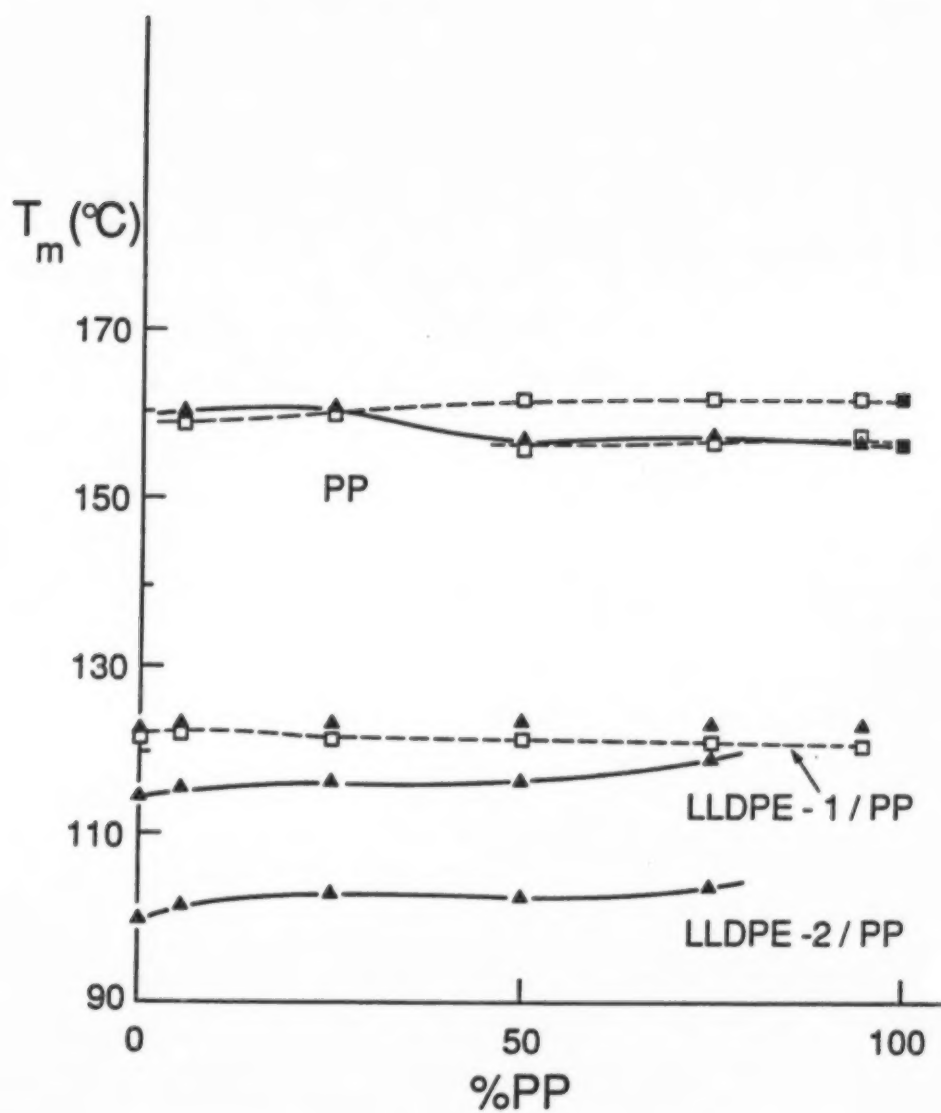


Fig. 12 Crystallization peak temperature as a function of composition for all materials.

multiple melting peaks. Fig. 12 shows two series of curves corresponding to the peak melting temperatures for all materials. The upper series illustrate the melting behaviour of the PP in both types of blends while the lower one include one curve for LLDPE-1 and three that correspond to the different melting peaks of LLDPE-2. In all cases the variation in peak temperature with the composition is small. While the melting peaks can easily be related to each component in the blend, all the materials cooled from 250 °C at a rate of 40 °C/min showed only one crystallization peak, T_C , with a broad low temperature shoulder for the compositions in LLDPE of 50% or more. For the pure resins, the crystallization temperatures were $T_C = 104.6$ for PP, 103.5 for LLDPE-1 and 93.8 °C for LLDPE-2. It is therefore not surprising to see only one peak for the blends, especially for system 1.

On the basis of the DSC (see Figs. 9 and 10) as well as DMTA scans it is evident that the two LLDPE are structurally different. While the temperature dependence of the loss modulus for LLDPE-1 (curve 1 in Fig.5) shows two dissipative peaks at $T_{\alpha} = 38$ °C and $T_{\beta} = -111$, that for LLDPE-2 (curve 1 in Fig.6) shows a shoulder at $T_{\alpha} \approx 35$, and in addition $T_{\alpha'} = -27$ and $T_{\beta} = -115$ °C. These results relate well to the values of -20 and -120 reported by Saini and Shenoy (16). The extra dissipative peak at $T_{\alpha'}$ indicates a more complex viscoelastic behaviour for LLDPE-2, responsible for usually better mechanical properties at or above ambient temperatures. The more complex molecular structure of

LLDPE-2 could also be inferred from multiple melting peaks in Fig. 10. While T_B originates in the amorphous phase and as such is related to the glass transition temperature, T_g , T_α and $T_{\alpha'}$ are associated with the amorphous phase in the vicinity of crystals, and as such are sometimes called pre-melting peaks (15). For PP (curve 7 in Figs. 5 to 8) there is a broad shoulder at $T_\alpha \approx 90$ and $T_B = 3^\circ\text{C}$. In short, at ambient temperature both polymers are above T_g and can be considered as viscoelastic liquids containing crystalline filler.

Returning to the tensile behaviour (Figs. 1 to 4), the lower modulus and enhanced ductility of PP containing 5% LLDPE can be viewed as a result of the lower crystallinity of the specimens in comparison to the expected additivity. The effect is particularly pronounced in the matrix dictated ϵ_B (the modulus of semicrystalline polymers above T_g can be described in terms of a liquid/solid composite structure).

It should be noted that the examination of the morphology clearly showed the presence of two phases for all blend compositions. The large negative deviation from additivity for ϵ_B indicates poor interfacial properties at high strains between the amorphous PE/PP phases. This poor adhesion between the domains in the blend is already visible at yield as is clearly shown by ϵ_y in Fig. 3. It should be noted that ϵ_y shows no sign of increased ductility for PP rich compositions which contrasts with the ultimate strain in Fig. 4.

The modulus, E , composition dependence of both blend systems can be described in terms of the Kerner equation (17):

$$E/E_m = [\alpha\psi E_i + B(1-\psi)] / [\alpha\psi E_m + B(1-\psi)] \quad (2)$$

where:

$$\alpha = 15(1-\nu_m)$$

$$B = (7-5\nu_m)E_m + (8-10\nu_i)E_i$$

with ν being the Poisson's ratio, ψ the volume fractions of inclusions and subscripts m and i indicating matrix and inclusions respectively. In the calculations, $\nu(\text{PE}) = 0.48$ and $\nu(\text{PP}) = 0.43$ were used (18). Numerical analysis indicates that experimental results for blends rich in PE follow the equation (2) quite well. However, to approximate the data for PP-rich blends, $\nu_m = 0.8$ (instead of 0.43) must be assumed. There is no justification for this.

For composites, the upper and lower bounds of modulus are written as (19,20):

$$E = \psi E_i + (1-\psi)E_m \quad (3)$$

and

$$E = [\psi/E_i + (1-\psi)/E_m]^{-1} \quad (4)$$

respectively. The relations describe situations where the tensile force is acting in the direction of reinforcements, Eq. (3), or perpendicularly to it, Eq. (4). The curves computed from these relations are shown in Fig. 1.

It is apparent that the concept of upper and lower bounds is successful in interpreting the results for PE/PP blends. PP, with its higher modulus, must be considered the reinforcing phase. Since, for high volume fraction, $\psi(\text{PP}) >$

0.5, PP forms the continuous phase, it is expected that the upper bound (Eq.(3)) will be obeyed. On the other hand, for low $\phi(\text{PP})$, where the "reinforcing" phase is discontinuous, the lower bound (Eq.(4)) should be applicable. Fig. 1 shows this, indeed. There are deviations from the general trend, e.g. E of blends containing 75 wt% of PP is higher than predicted by Eq.(3) while E of blends containing 95% of PP is lower, but, as indicated in Fig. 11, these deviations are probably due to variation of crystallinity. In short, the low strain mechanical behaviour of LLDPE/PP blends can be adequately described in terms of the composites model.

As demonstrated in Figs. 2 to 4, the higher strain blend properties show negative deviations; the higher the strain, the larger the deviation. While the yield phenomena may barely be approximated by the lower bound, the maximum strain at break, with its $\epsilon_b(50\%) < \epsilon_b(\text{PP})$, would require incorporation of a negative interfacial contribution (5).

In most engineering applications the stresses are calculated to be well below yield. The uncompatibilized blends considered in this work can provide an adequate performance with properties that can be approximated by Eqs. (3) or (4).

FINAL COMMENTS

There is a significant difference in behaviour between PP blended with LLDPE and with low density polyethylene, LDPE. As shown by Nolley, Barlow and Paul (5), addition of a

compatibilizer was a must in the PP/LDPE system. On the other hand, our results on PP/LLDPE (13,15) confirmed by the data presented here indicate that the low strain mechanical properties of non-compatibilized blends are nearly additive, independently of the melt viscosity ratio of the components.

The composition containing 5% PE shows a particularly attractive behaviour. A decrease in the total crystallinity of the system is considered responsible for this behaviour.

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**POLYSTYRENE-POLYETHYLENE MELT BLENDS
OBTAINED THROUGH
REACTIVE MIXING PROCESS:**

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POLYSTYRENE-POLYETHYLENE MELT BLENDS OBTAINED THROUGH REACTIVE MIXING PROCESS:

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ABSTRACT.

Polystyrene (OPS) and polyethylene (CPE) with oxazoline and carboxylic acid functionality, respectively, were melt blended in a Rheomix mixer under a variety of conditions. The properties of these blends were examined and are correlated with the compositions and mixing conditions such as shear rate, time and temperature. Torque measurement indicate that an increase in torque is observed which is believed related to chemical reaction between OPS and CPE. The difference between the maximum and minimum torque ($T_{max}-T_{min}$), increases from 48 to a maximum of 510 m-g for 10 and 40 % CPE reacted blends, respectively. But on further increase in the CPE amount in the blend the torque drops reaching a final minimum value of 133 m-g for a blend with 90 % CPE. Differential Scanning calorimetry (DSC) studies reveal a single first order transition for each of these polymer blends. Furthermore, evidence of the glass transition temperature for OPS diminishes with increasing CPE content and mixing time. Scanning electron micrographs (SEM) show a fine dispersion in these reactive blends, with particle size much smaller than a micron. Blends with 50 % or more CPE have no distinguishable features as such. Mechanical properties such as elongation at break of reacted blends are improved over the nonreactive polyethylene(PE) and polystyrene (PS) blends. An intermolecular reaction between the

OPS and CPE results in a graft polymer, which imparts improvement in the overall properties of these reacted blends. The maximum grafting reaction corresponds to 40 % CPE blend, which is being evaluated as a potential compatibilizer.

INTRODUCTION.

In recent years a major improvement in impact properties of polymer blends has been reported in those cases where some type of chemical reaction can be expected during the melt mixing stage. A major portion of this type of work is related to toughening of nylon [1-3]. Various functionalized elastomers were added to this plastic, and as a result of reaction between the functional groups of the elastomer and the amine end groups of the nylon, blends of superior impact properties have been obtained. Similar results were reported when instead of elastomer, polyethylene with acid functionality [4], and polypropylene with anhydride groups [5], were blended with nylon. A hot oil resistant thermoplastic elastomer based on functionalized polyolefines and amine terminated nitrile-butadiene rubber was obtained on melt mixing of these polymers and this particular improvement, too, was attributed to the intermolecular reaction [6].

This procedure of reactive mixing processing for obtaining blends of improved physical properties offers a number of advantages over the previously used methods. For instance, the processing equipment is being used as a reactor, variables such as temperature and pressure can be controlled, it excludes the requirement of a compatibilizer, and since it is done in the molten state, this technique has the potential to be cost effective.

In many cases a chemical reaction between the matrix and dispersed phase improves adhesion, but this is only one of the criteria for improving polymer properties. Controlled interfacial energy,

critical domain size, and interparticle distance are some of the other factors, which are considered to determine the ultimate physical properties of the blends. Recently it has been proposed that for some systems toughness can only be achieved if the interparticle distance is smaller than a critical value [1]. There are hardly any detailed studies on the toughening of polystyrene by a reactive processing technique without using a compatibilizer, though efforts have been made to toughen polystyrene through a lewis acid initiated melt reaction with EPDM rubber[7]. Functional polymer blends of polyolefines/vinyl polymers are reported to have good mechanical properties, but information on their preparative procedure is lacking [8], and very little can be found on polystyrene/polyethylene reacted blends. The publication of articles [9-11] relating to the reactive polymer processing have elaborated on the significance of the method and also listed a number of functionalized polymers including reactive polystyrene with oxazoline functionality. In our previous study [12] we investigated various aspects of the coupling reaction between OPS and CPE. Here the influence of mixing conditions on mechanical, physical, and morphological properties of OPS-CPE reacted blends is being investigated.

EXPERIMENTAL.

Reactive polystyrene(OPS), reactive polyethylene(CPE), low density polyethylene(PE) and polystyrene (PS) were obtained from Dow Chemical Co. OPS had 1 mole % oxazoline functionality, whereas the carboxylic acid concentration in CPE was 9 mole %. Irganox 1010 was used as an antioxidant in all the blends unless mentioned

Table 1 :- OPS-CPE reacted melt blends prepared under various conditions.

Sample No	CPE (wt %)	Temperature C°	Mixing Time minutes	Speed RPM
1	10	225	30	100
*1A	10	225	30	100
2	20	225	30	100
2A	20	180	30	100
2B	20	250	30	100
3	30	225	30	100
3A	30	225	10	100
3B	30	225	60	100
4	40	225	30	100
4A	40	225	30	50
4B	40	225	6	150
4C	40	225	11	150
4D	40	225	16	150
4E	40	225	30	150
5	50	225	30	100
6	60	225	30	100
7	70	225	30	100
8	80	225	30	100
9	90	225	30	100

* Sample 1A contained no antioxidant.

otherwise.

Polymers were melt blended on a Haake-Buchler Rheomix mixer Model 600. The mixer was set at the required temperature, time and speed. Once the temperature was achieved, the dry mixed polymers were fed into the mixer. After the melting of the polymers 0.1% antioxidant was added to the melt, and mixing was continued for the set time. Temperature and torque were recorded as a function of time. At the end, the melt was immediately collected and was used in characterization work. Reacted blends prepared under various conditions are listed in Table 1. Blends of non reactive polymers (PS/PE) were blended under similar conditions.

Subsequently, films of various thicknesses were pressed at 170°C for four minutes, and were used for DSC and tensile testing. DSC thermograms of polymers, and their reacted and unreacted blends were recorded on a Perkin-Elmer differential scanning Calorimeter, Model DSC-2C. The instrument was calibrated with indium. Circular discs of polymers, weighing 2-5 mg, were cut from the films and were crammed in aluminum pans. Their thermograms were recorded at a heating rate of 20°K /minute in the region of 300-500°K.

For SEM studies, samples of 2-3 mm diameter were fractured under liquid nitrogen, were gold coated and then their micrographs were taken on a scanning electron microscope, JOEL Model JSM 840. The magnification range was varied according to the nature of the material.

Ultimate elongation measurements were made on an Instron testing machine Model 122 at an extension rate of 5 cm /minutes. Test

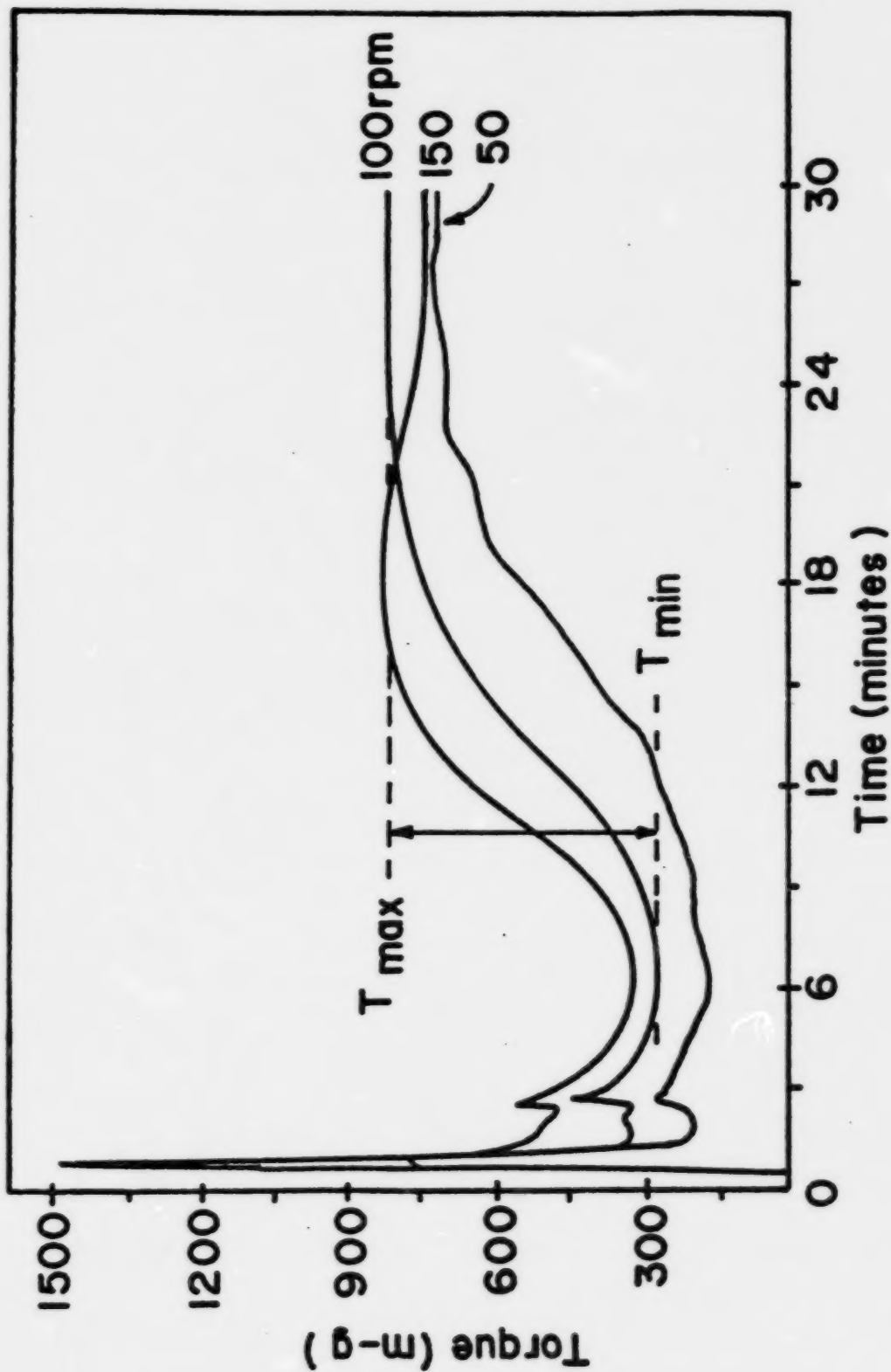


Figure 1: Time-torque relationship for OPS-CPE (60/40) reacted blend at different mixing speeds.

samples of $20 \times 2 \times 0.025$ cm dimension were cut from films of uniform thickness. A maximum of five specimens of each sample were used and average values of ultimate elongation were obtained. Impact tests on these polymer reacted blends were performed on a Gardner Impact Tester, but only blends containing 30 % CPE or less could be tested as others did not show a clear fracture with the range of weights available.

RESULTS AND DISCUSSION.

It has been noticed that blends with some type of specific interactions can be distinguished from blends with no such interactions, through their melt viscosity characteristics [13]. On the same grounds some type of correlation can be expected between the torque and the nature of the blends and can be evaluated during the melt mixing stage. Typical torque-time curves for OPS-CPE (60/40) blends, mixed at three different speeds, are shown in Figure 1. The initial sharp rise and drop in torque corresponds to the melting of the polymers, then a small increase in torque is noticed when the antioxidant is added. Between 5-8 minutes period the polymers are intimately mixed and this region shows a minimum torque (T_{min}). It is followed by a rise in torque, which ultimately reaches a maximum value (T_{max}). This region is believe to correspond to the time when chemical reaction occurs between the two polymers. Subsequently the blend is homogenized. The position of these curves, obviously, changes with the mixing speed. No such increase in torque was noticed when unreactive polymers(PS/PE) were blended together. A majority of the reacted blends were blended at 225°C and a mixing speed of 100

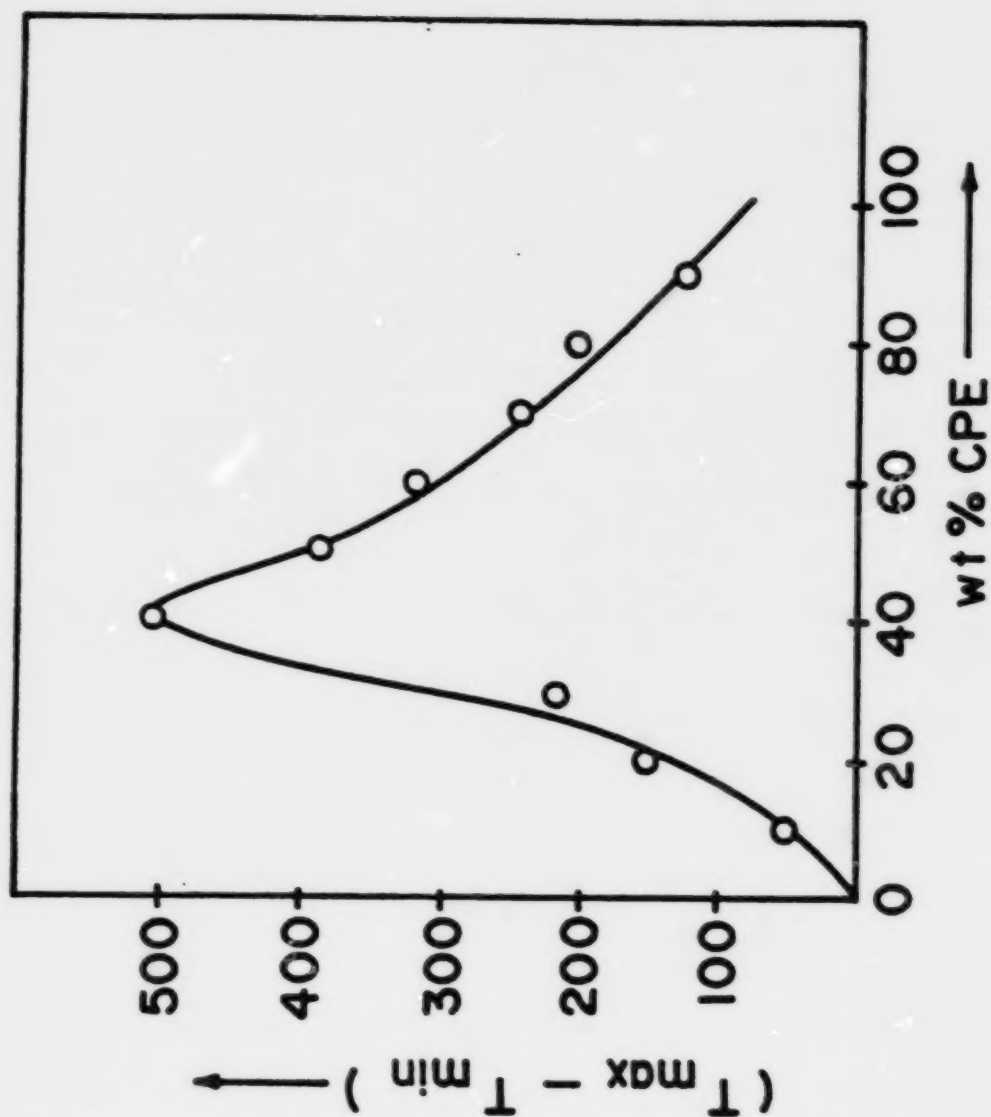


Figure 2: Torque changes vs reacte blend composition.

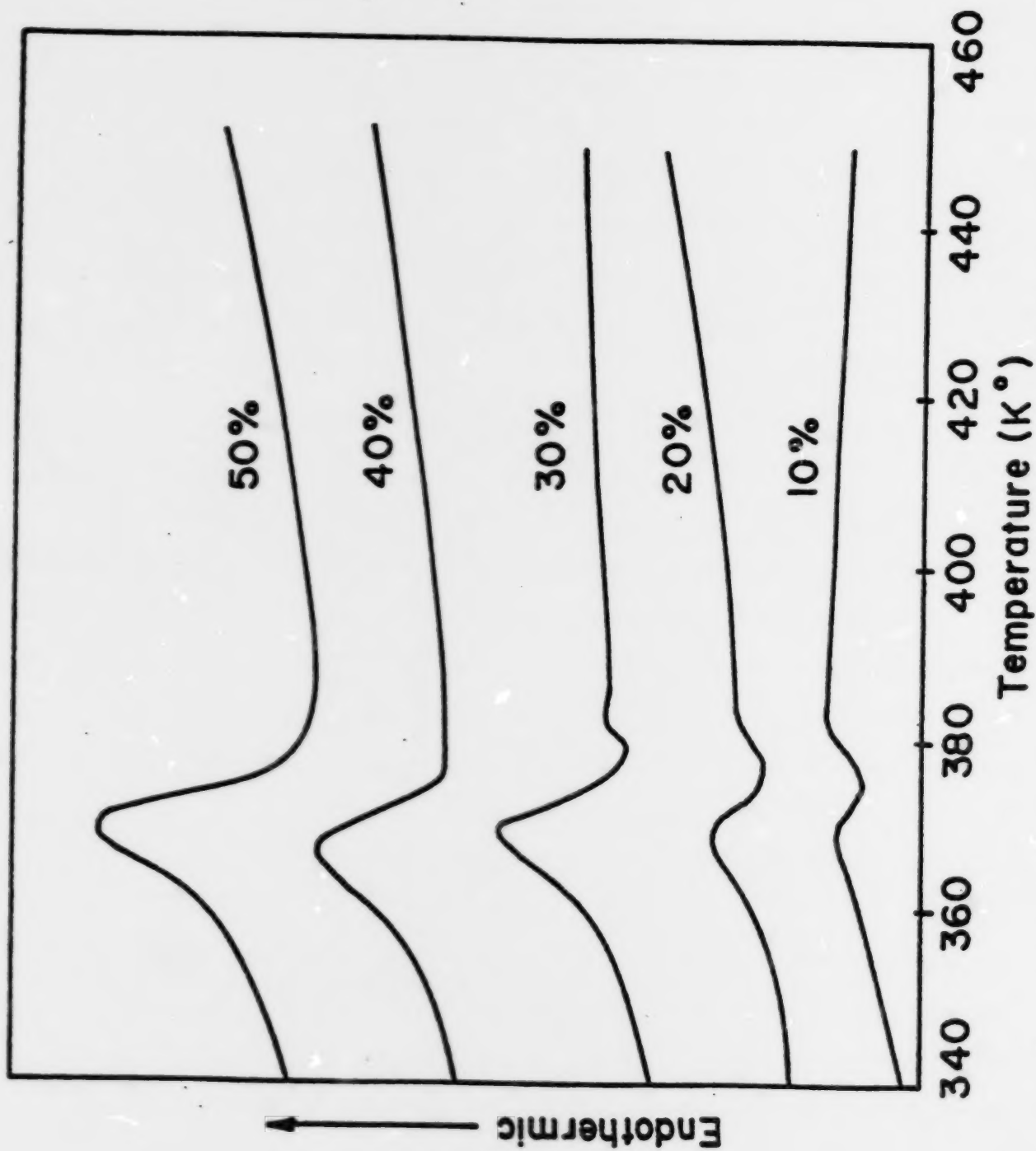


Figure 3: DSC thermograms of various OPS-CPE reacted blends.

Numbers indicate the weight % of CPE.

RPM. Three runs were made for each composition under these conditions and an average value of $(T_{max}-T_{min})$ was computed. These averages vs composition are plotted in Figure 2. There is a substantial rise in torque for the 40% CPE composition, and a change in physical properties as well. For instance, the flow characteristics of this reacted blend were different from other compositions, which made it difficult to get thick films by ordinary pressing method.

This reacted blend, most probably, consists of varying amounts of the OPS-CPE graft polymer. In Figure 2 the maximum point corresponds to a composition where the molar concentrations of the carboxylic acid groups and oxazoline groups are 3.6 and 0.6 %, respectively. This suggests that at this proportion of 6:1 a maximum amount of the coupled polymer is formed, which results in the maximum effect on viscosity and possibly other physical properties. Proportions of CPE on either side of the 40% result in less coupled polymer and lower torque.

More information on the nature of these reacted blends was obtained from DSC data, which substantiate our findings from torque. Thermograms of a few reacted blends are shown in Figure 3. The melting point of CPE and glass transition of OPS were found to be 370 and 379°K, respectively. The difference between the thermograms of OPS-CPE reacted and dry blends were explained somewhere else [12]. It can be seen in Figure 3 that thermograms of blends with 30 % or less CPE have melting peaks around 370°K, and also there is a slight indication of glass transition temperature of OPS near 380°K. From this it can be deduced that the components

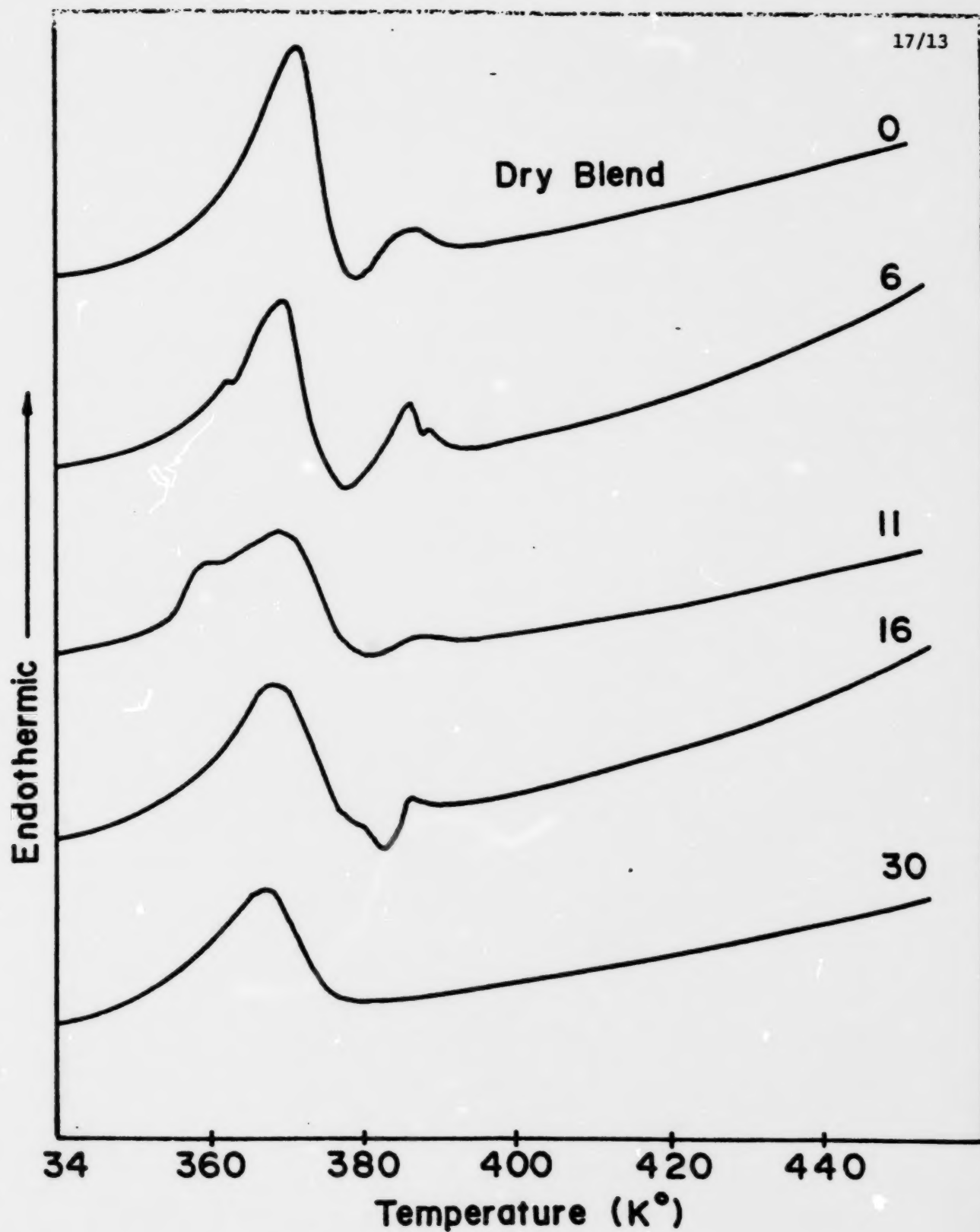


Figure 4: DSC thermograms of OPS-CPE (60/40) reacted blends mixed for times (minutes) indicated on the thermograms. Zero time refers to a dry blend.

of these blends are not completely coupled. This was confirmed when soluble material was extracted out with toluene and was found to be OPS. In the case of the 40 % CPE composition there is no indication of glass transition temperature and no OPS could be extracted with toluene. This, too, provides support for the view that this particular blend is mainly OPS-CPE graft polymer. A more pronounced melting peak for reacted blends with higher CPE content shows the excess of CPE.

There is not an easy method for evaluating the kinetics of this coupling reaction. Yet the mixing of these two polymers at a higher speed for different time intervals, can provide some information. This was done with the OPS-CPE (60/40) system, and the resulting thermograms of these melt blends are compared with a dry blend in Figure 4. Both the dry blend and the melt blended samples mixed for 6, 11, and 16 minutes, have the characteristics of an immiscible two component system with a marked melting peak and a glass transition region. With an increase in the time of mixing the sharpness of the melting peak tends to reduce and becomes broader. Only after 30 minutes does the glass transition temperature associated with OPS disappear. Since the heat changes associated with the glass transition region are very small and can be influenced by a number of factors, no reliable quantitative estimates can be made from this region. Relatively larger heat of fusion (ΔH) for the OPS-CPE system allows for quantitative estimates to be made. The reproducibility of ΔH estimates for OPS-CPE system were checked in a related work and were found to be satisfactory. The ΔH for

CPE itself is 55.5 J/g , which reduces to 17.1 J/g for a dry mixed blend of 40% CPE composition. On melt mixing this particular blend ΔH gradually decreases with an increase in the time of mixing. These values are 16.3, 15.1, 14.2 and 12.1 for the reacted blends mixed for 6, 11, 16, and 30 minutes, respectively.

Calculations based on the original value of ΔH for CPE should give a value of 22.2 J/g for 40% CPE composition, but the actual values obtained for the dry and reacted melt blends are lower than this; it means mixing results lowering of ΔH in each case.

Although physical mixing in dry, results in lowering of ΔH , no substantial change in the sharpness of the peak is noticeable (Figure 4), whereas melt blending results in the broadening of the peak and eventual disappearance of the glass transition temperature after 30 minutes. This indicates that the decrease in ΔH during melt blending is due to the grafting reaction, which reduces the mobility of the CPE chain and hence decreases the overall crystallinity in the blend. This decrease in the heat of fusion may be considered as an indicator of the grafting reaction. Some reacted blends of the same composition were mixed at three different temperatures of 180, 225 and 250°C; and from their color variations it was thought that these blends may have different characteristics. However, their DSC thermograms were found to be identical, so no further work was pursued on this aspect. This suggests that the coupling reaction is not limited by chemical kinetics but rather by mass transfer consideration. The remaining reacted blends were mixed at just one temperature of 225°C and for 30 minutes. It was also noticed that the presence or

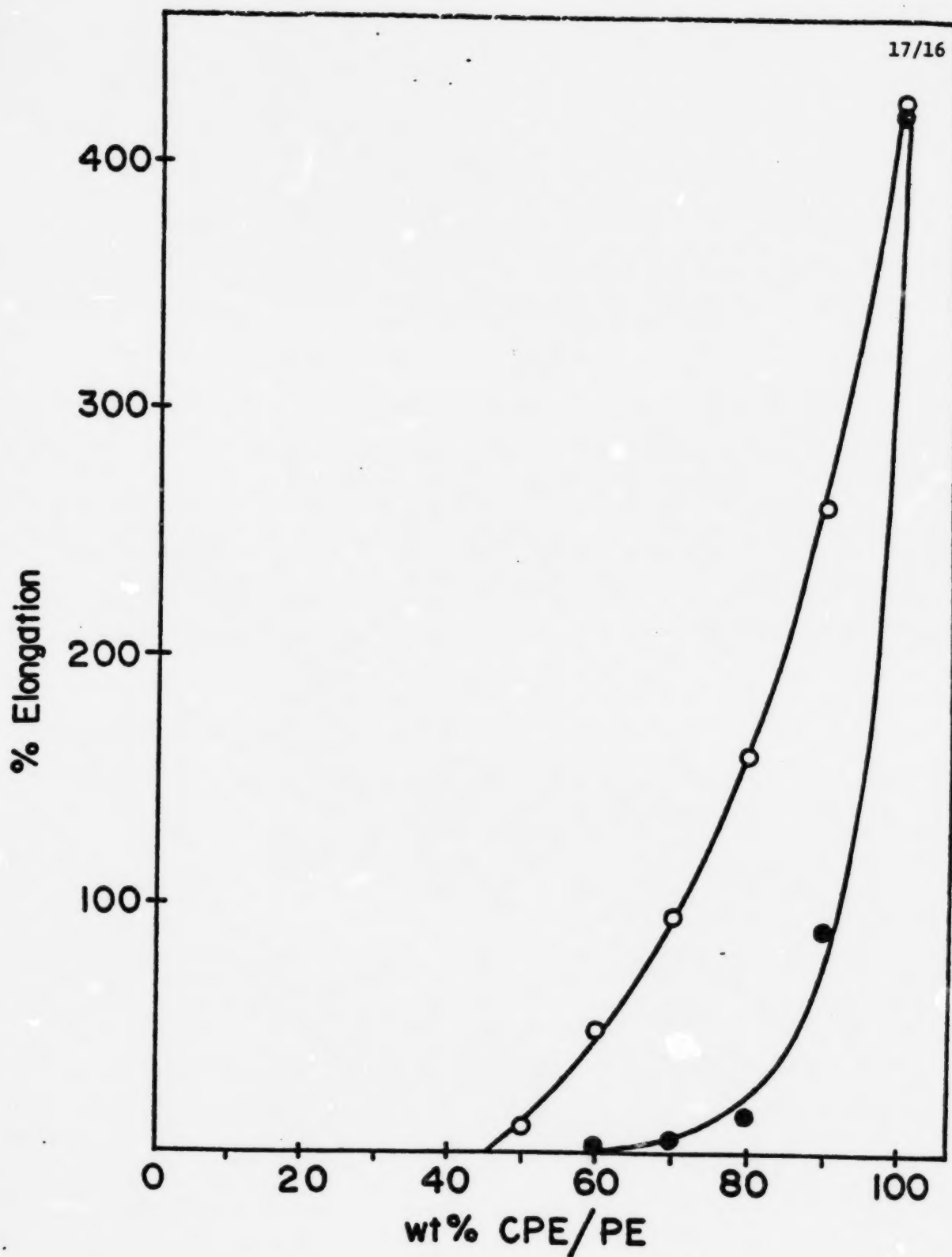


Figure 5: Elongation at break vs composition of reacted (○) and unreacted (●) melt blends of polystyrene and polyethylene.

absence of antioxidant did not affect the thermal properties of the reacted blends.

Elongation at break of OPS-CPE blends and PS-PE blends were measured over the full composition range. A substantial increase in elongation occurs after 50 % CPE has been added to the blend, and can be seen in Figure 5. It is interesting to note that improvement in elongation takes place only after surpassing the maximum torque region in Figure 2. In an earlier work the mechanical properties of PS/PE blends were improved by substituting 5 to 10 % PE with PS-PE graft copolymer in PS rich blends[14]; and the improvement was attributed to the emulsifying effect of the copolymer. In this work the improvement in mechanical properties is the result of chemical reaction between OPS and CPE, and compared to the above the effect is not very substantial.

Gardner impact tests on 10, 20 and 30 % CPE reacted blends showed no significant improvement in the impact properties for these blends. Generally, it is understood that a certain concentration of the dispersed phase is necessary for absorbing impact energy. No evidence of improvement for 10 % CPE blend may be justified this way. However, despite chemical reaction, the lack of any improvement at 20 and 30% CPE was surprising. This may be attributed to the insensitivity of the impact test method. It had been shown in earlier work that PS becomes tougher at low concentration of PE, provided small amounts of graft and especially block copolymers are added to this blend [14-17]. Fayt et al have pointed out that the use of copolymers as

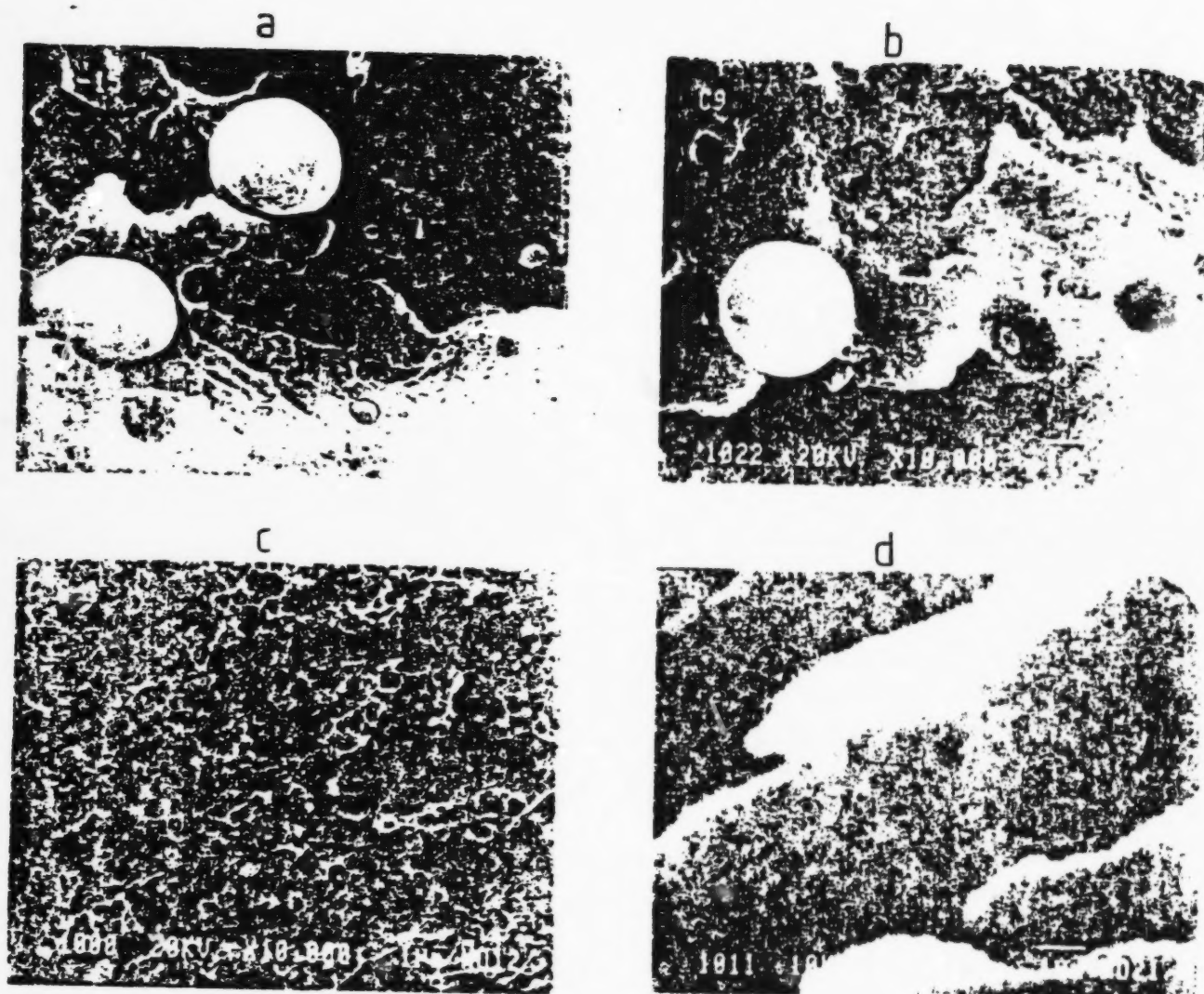


Figure 6: SEM micrographs of a) PS-PE (90/10), b) PS-PE (10/90), c) OPS-CPE (90/10) and d) OPS-CPE (10/90).

emulsifiers, result in a significant increase in both the strength and elongation of the PS rich PS/PE blends[17]. It was suggested that this increase was not only due to the improvement in interfacial adhesion but also due to the interlocked phase morphology. In other words, the role of the emulsifier is to decrease the size of the interlocked domains and to prevent the coalescence of the minor phase. For toughening polymers such as nylon with rubber, it has been strongly suggested that the interparticle distance is the only parameter which determines whether a blend will be tough or brittle [1]. Because of the relatively poor impact properties of this system scanning electron micrographs were obtained to observe the morphology and attempt to relate the structure to properties.

There is a marked contrast between the morphology of OPS-CPE reacted blends and that of PS-PE blends. Figure 6 shows micrographs of these compositions illustrating the compatibility and phase inversion. In micrograph (a) of Figure 6, PE is dispersed in PS, whereas the reverse is the case in (b). In both these cases the spherical shapes and smooth surfaces of the dispersed particles as well as that of the cavities left behind by them during the fracture, are typical features of an incompatible blend. Micrographs (c) and (d) depict the morphologies of the OPS-CPE reacted blends at the same proportions as for the unreacted blends. In micrograph (c), where CPE is dispersed as a minor phase in OPS, the incompatibility evident in (a) is much reduced, with domain sizes in the range of 0.1- 0.5 μ m in (c) compared to 1-5 μ m in (a). The finer dispersion is indicative of

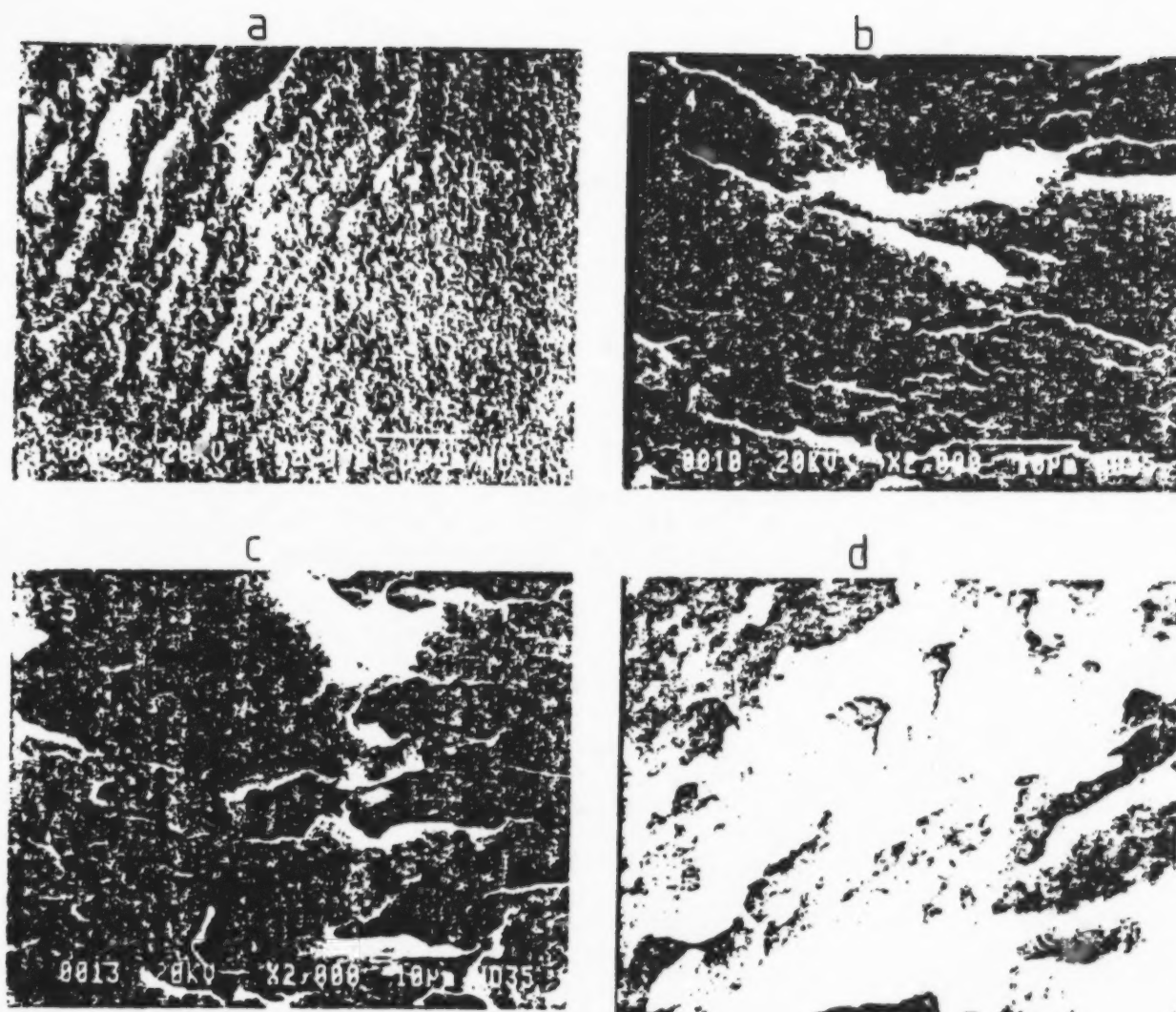


Figure 7: SEM micrographs of OPS-CPE reacted blends with
a) 30, b) 40, c) 50 and d) 70 wt % CPE.

good adhesion between the two phases. On phase inversion, when OPS becomes the minor phase, the phase distinction as such disappears and the blend appears to be homogeneous (d). It should also be taken into account that the amount of the grafted polymer expected to be formed, is based on the amount of the reactive groups available in the system. For example, if it is assumed that CPE and OPS react in 2:3 weight ratio, then a reacted blend containing 10 % CPE will have 25 % grafted polymer dispersed in OPS, and blend with 10 % OPS will contain about 17 % grafted polymer dispersed in CPE. Hence the micrographs in Figure 6 c) and d) will not be a case of simple phase inversion because in each case the amount of the grafted polymer will be different.

CPE rich reacted blends, fractured under liquid nitrogen, did not reveal microdetails at higher SEM magnification. However, at lower magnification general phase structure of these blends in a range of composition can be seen in Figure 7. Again, there is no sign of incompatibility. However, the nature of the fracture surface changes in the range of 30 to 70 % CPE blends (a-d). The blend with 30 % CPE has a very fine morphology (a), but it was poor in impact strength, which may be due to the absence of an appropriate domain size of the dispersed phase. The 40 % CPE composition corresponds to a region where the torque increase is at a maximum and the micrograph (b) does not show much phase distinction.

Micrographs (c) and (d) refer to CPE rich blends , which have better elongation and impact properties. This is likely explained in part by the fact that CPE has become the continuous phase and the PS inclusions are sufficiently spaced so as to have a reduced

effect on mechanical properties.

The effect of mixing time on morphology was also investigated for one particular blend with 40 % CPE, but micrographs did not reveal any difference with time.

These results show that by blending OPS and CPE interfacial adhesion has been achieved through the chemical reaction, but it appears that the reacted blends consist mainly of the grafted polymer plus the unreacted polymer. For instance, in the OPS rich blend the resulting fine grain morphology does not appear optimal for improving mechanical properties. It appears that for this purpose not only adhesion but morphology, too, has to be controlled.

CONCLUSIONS.

Reacted blends of polyethylene and polystyrene can be prepared by a reactive melt mixing process. These blends have significantly improved elongation over their unreactive counterparts. Despite very good adhesion, elongation at break and impact strength did not show any significant improvement in polystyrene rich reacted blends. This confirms earlier conclusion that good polymer/polymer adhesion is not the only factor necessary for toughening polymer blends; domain size and dispersed phase spacing likely play a significant role in this system. By diluting one or both of the reactive polymers there is a possibility of controlling domain size and consequently improving the mechanical properties to a larger extent.

Increased shear rate reduces the overall time required for reaction of this reactive blends. This indicates the possibility

of using a twin screw extruder or a specially designed single screw extruder to continuously process such blends.

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THE PHASE BEHAVIOR AND MECHANICAL PROPERTIES
OF POLYARYLATE AND POLYCARBONATE BLENDS

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ABSTRACT

The influence of blend composition and compounding conditions on the phase behavior and mechanical properties of polyarylate/polycarbonate blends were studied. The polymers are known to undergo ester-exchange reaction which may affect the phase behavior. The extent of transesterification depends upon the blend's thermal history. Single screw extrusion, twin screw extrusion, and solution casting were employed for blend preparation with varying thermal history.

When transesterification is minimal, the blends are only partially miscible. Two transition temperatures, corresponding to a polycarbonate rich phase and to a polyarylate rich phase, were seen in solution cast blends and in blends that were extruded (single screw) at 285 C. When the exchange reaction is advanced (twin screw and higher extrusion temperatures), the blends become miscible as evidenced by a single T_g .

The flexural and tensile properties of blends that were prepared in a twin screw extruder show a small positive synergism. The impact properties, on the other hand, show a pronounced negative synergism, probably the result of advanced exchange reaction and thermal degradation. If the exchange reaction is not contained, the blending of polycarbonate and polyarylate does not appear to result in a material with improved mechanical performance.

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study, good housekeeping and scientific procedures were rigorously maintained, but optimization of extrusion conditions and the use of additives to stabilize the blends, were not attempted.

A blend of 50/50 PC/PAR was also prepared in a laboratory size, single screw extruder (Haake, 3/4 inch) at three temperatures: 285, 305, and 325 C. A film of a 50/50 blend was also cast from methylene chloride solution. The extruded blends were subsequently injection molded to produce tensile, flexural, and impact test specimens.

Blend Testing

The tensile and flexural testing was done on an Instron machine following ASTM testing procedures. The notch Izod was done on a Tinius Olsen pendulum, according to ASTM D 256-73. Direct impact of plaques was done on a Dynatup instrumented drop tower machine, using 5 cm (2 inch) support ring and 1.25 cm dart. Impact velocity was 3 m/s and the temperature -29 C (-20 F). Differential scanning calorimetry (DSC) was done on a Mettler model TA3000 with DSC30 measuring cell. The samples were scanned from room temperature to 220 C at 5 C/min. Molecular weight was determined by gel permeation chromatography technique using Water Associates instrument (150-C ALC/GPC). Column arrangement consisted of five μ -Styragel columns in series, with permeability limits of 10^5 , 10^4 , 10^3 , 500, and 100A. Narrow molecular weight distribution polystyrene samples were used for calibration.

INTRODUCTION

Polyarylates are a family of aromatic polyesters which are based on aromatic dicarboxylic acids and diphenols. The present commercial polyarylates are the product of the reaction of bisphenol-A and iso/tere (50/50) phthalic acids. A review on polyarylates was published recently by Maresca and Robeson⁽¹⁾. Blends of polyarylate with various polyesters⁽²⁻⁴⁾ and with polycarbonate⁽⁴⁻⁷⁾ have been studied in some detail with regard to phase behavior. Taking the glass transition temperature as the criteria for miscibility, blends of polyarylate (PAR) and polycarbonate (PC) were reported to be miscible^(5,6), as well as immiscible^(4,7). A plausible explanation to this discrepancy is ester exchange between PAR and PC which results in copolymer formation and improved miscibility⁽⁴⁾. This explanation is supported by a recent study of that reaction by Devaux et al.⁽⁸⁾

Very little has been reported on the mechanical and physical properties of polyarylate blends. The tensile properties of a series of polyarylate blends with polycarbonate was studied by Mondragon and Nazabal⁽⁹⁾, who reported a positive synergistic effect with the modulus and tensile yield strength maxima at a ratio of about 50/50 by weight. If such positive synergism were to extend to other properties, particularly impact strength, it would be beneficial to blend PAR with PC, since the Izod impact strength of PC is four times that of PAR.

The objectives of the study described here were twofold. The first was to generate additional data on the phase behavior of PC and PAR blends, emphasizing the influence of the compounding conditions. The second objective was to investigate the mechanical performance of PC/PAR blends.

EXPERIMENTAL

Blend Preparation

The polycarbonate used is a commercial product of the Dow Chemical Company: Calibre 300-15. The T_g of this product by thermal analysis (DSC) is 148 C. The polyarylate is a product of AMOCO: ARDEL D-100. It has a T_g of 194 C. The resins were used as received. Prior to compounding, they were dried in a vacuum oven, at about 120 C, for at least 24 hr.

A series of PC/PAR blends, with varying ratio of PC and PAR, were prepared in a twin-screw extruder (Werner Pfleiderer, 30mm). The operating conditions are listed in Table 1. The temperature settings along the barrel and at the die were kept relatively constant. But the output and hence, the residence time in the extruder, varies with the blend composition. The output depends on the viscosity of the blend (the starve-fed extruder was operated at 100% of torque) which increases with PAR content. Consequently, thermal degradation and exchange reaction are, probably, more advanced in the PAR rich blends. At this point it should be stated that melt blending requires special and, sometimes, elaborate precautions (optimization of compounding conditions, addition of antioxidants and stabilizers, etc.) to produce a useful material. In this

TABLE 1
Compounding Conditions on Twin-screw Extruder
(Werner-Pfleiderer Model 30)

Composition PC/PAR	Temperature Setting, C					Output lb/hr	Blend M_n
	Zone: 1	2-3-4	5	6	Die		
15/85	260	290	280	250	302	8.6	13,870
30/70	260	290	280	260	306	9.2	13,520
50/50	260	290	280	260	302	9.8	14,720
70/30	260	290	280	260	300	13.9	15,790
85/15	260	290	280	260	300	18.1	15,620

PC's M_n = 15,900

PAR's M_n = 19,560

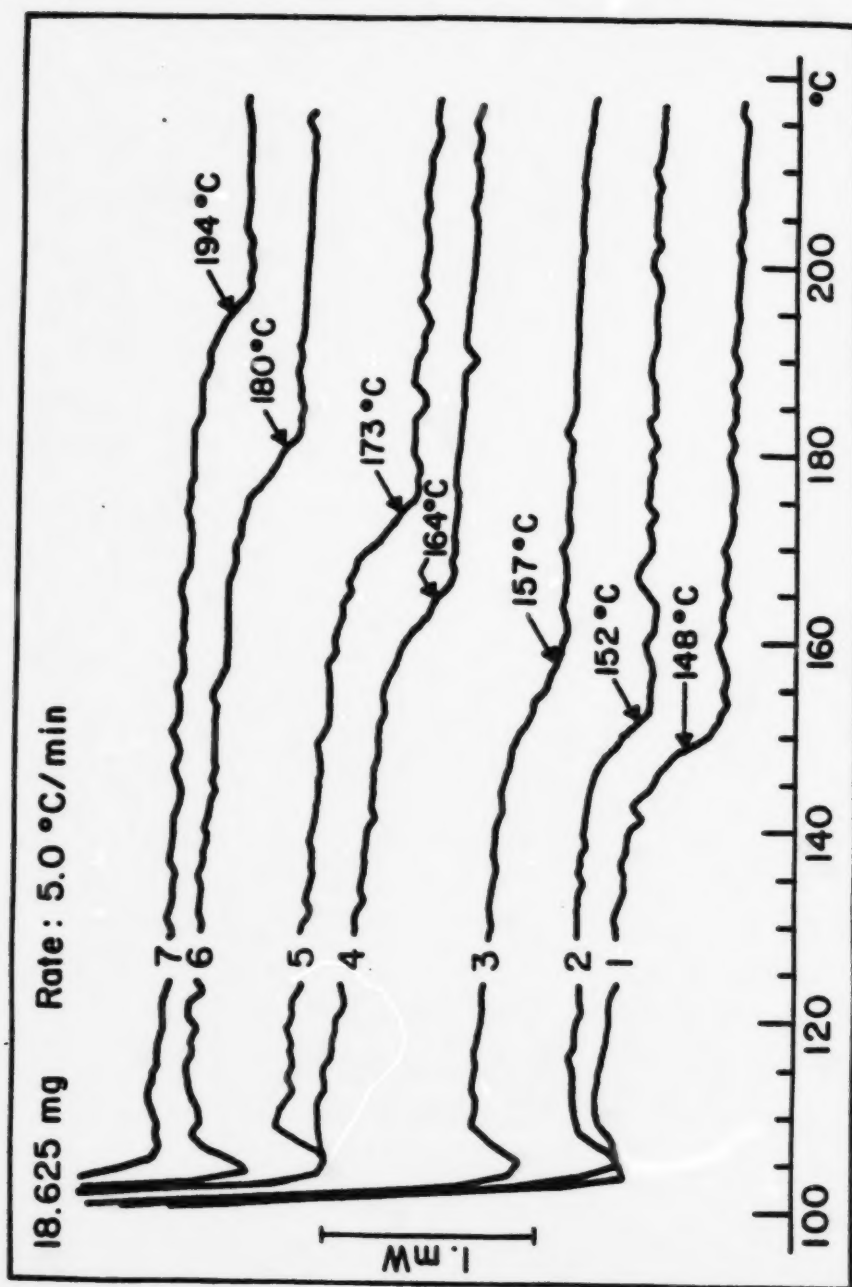


Figure 1. DSC curves of polycarbonate, polyarylate, and twin screw PC/PAR blends: 1) 100% PC, 2) 85% PC/15% PAR, 3) 70/30, 4) 50/50, 5) 30/70, 6) 15/85, 7) 100% PAR.

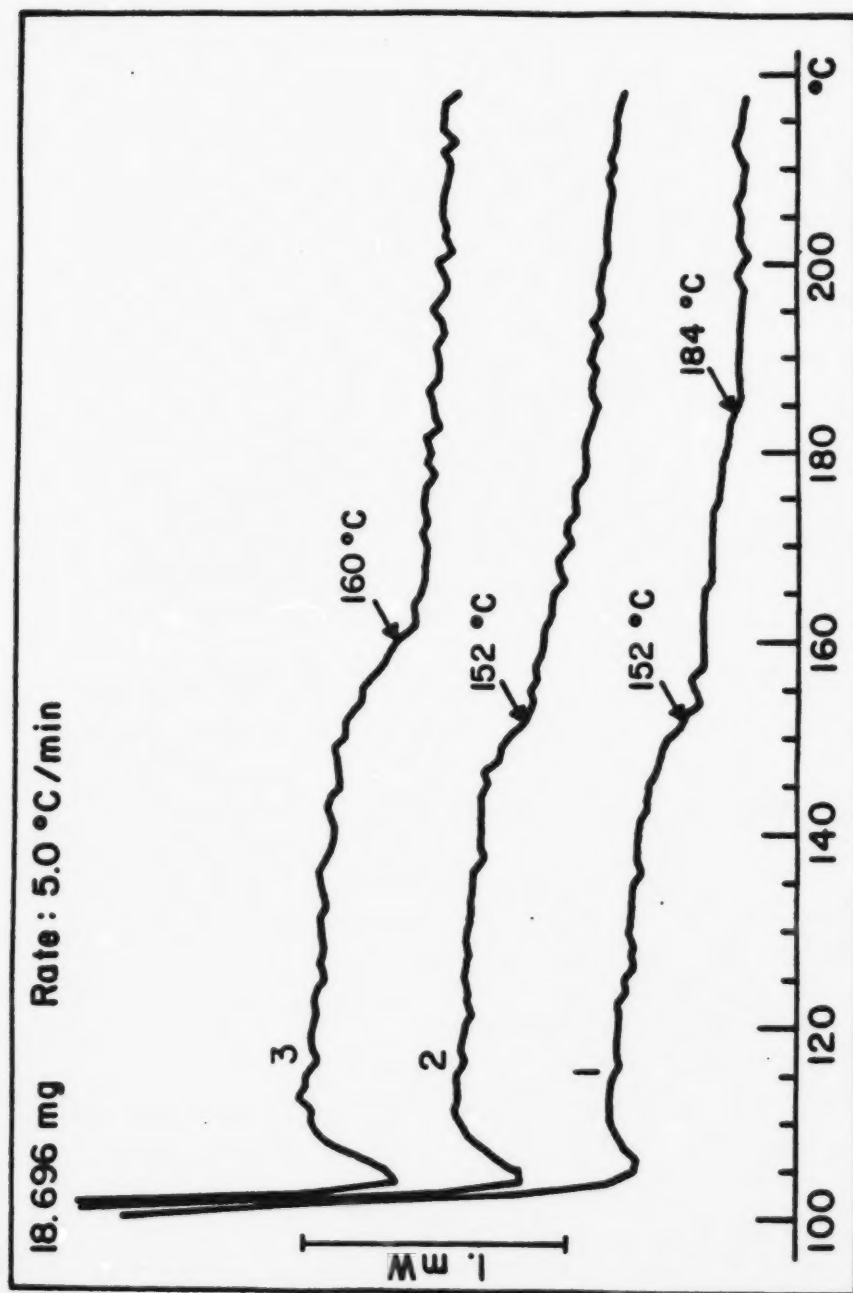


Figure 2. DSC curves of single screw PC/PA6 blend (50/50) extruded at: 1) 285 °C, 2) 305 °C, and 3) 325 °C.

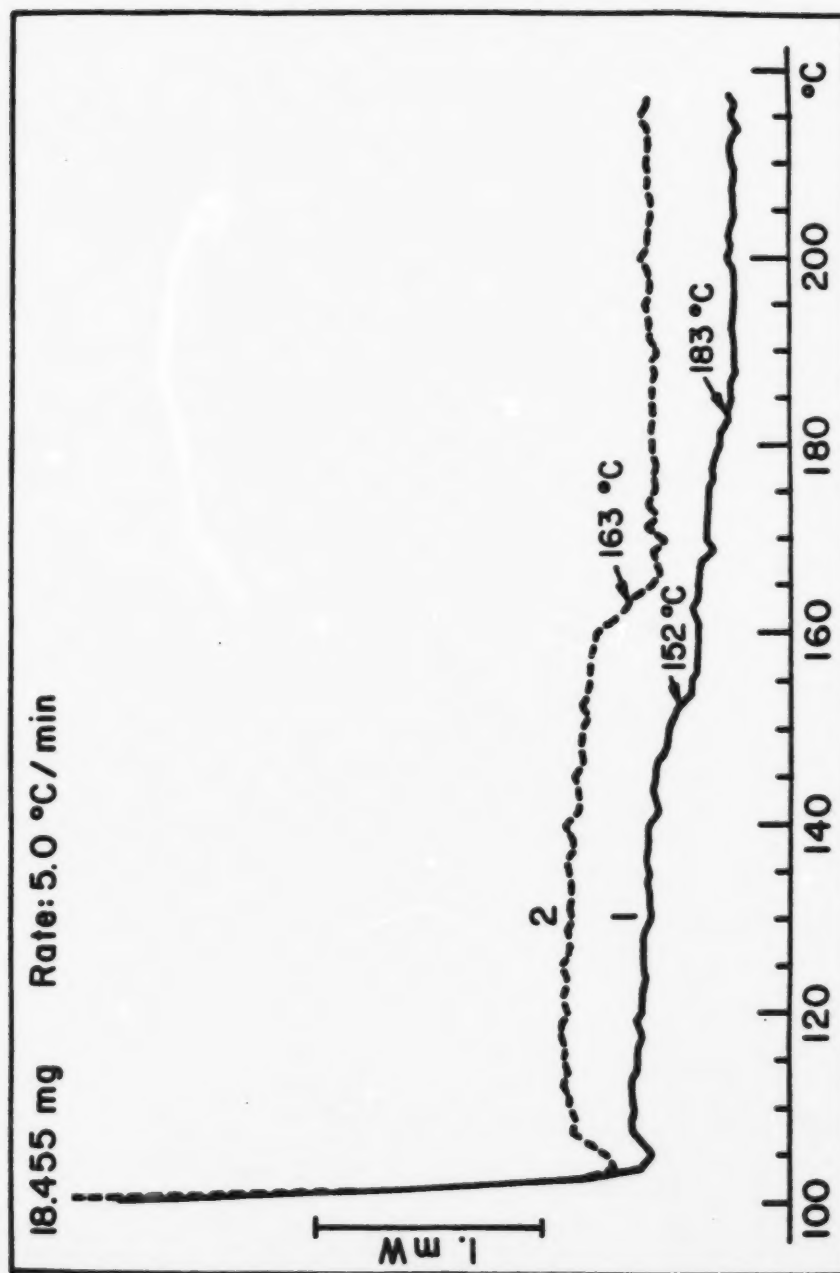


Figure 3. DSC curves of 50/50 PC/PAR blends: 1) resins dissolved in methylene chloride at 23 °C and cast into a film.
2) twin screw extrudate dissolved in methylene chloride and cast into a film.

RESULTS AND DISCUSSION

I. Blend Characterization

All the blends, prepared by the twin-screw extruder, were transparent, regardless of composition. Their basic color was yellow, turning to dark yellow-brown in the PAR rich blends, and to very light yellow in the PC rich blends. The development of the brown color is, probably, the result of some degradation which occurred during blending. That degradation did take place is evident from the molecular weight data (GPC), listed in the last column in Table 1. It is apparent that the molecular weight of the various blend composition is below expectation (assuming no degradation), and is more so in the PAR rich blends which experienced longer residence time in the twin-screw extruder. Consider, for example, the first composition in Table 1, which contains 85% PAR and was the most difficult to process because of the high melt viscosity of the PAR. The resultant M_n of that blend was found to be 13,870 compared to a calculated value of 18,900, assuming no change in the molecular weight of the parent polymers during compounding. By contrast, when a mixture of the pellets of the two polymers, with the same composition, was injection molded directly (i.e. without first melt-mixing) in a reciprocating-screw injection molding machine, the resultant M_n of the molded specimens was found to be 18,400. Incidentally, these specimens were also transparent (the plasticizing screw obviously provided some degree of compounding), but with a much lighter color than the melt-mixed composition.

DSC plots of PC, PAR, and the five blends, prepared in the twin-screw extruder, are shown in Figure 1. The T_g of PC and PAR, taken to be at the inflection point, are 148 and 194 C, respectively. All the blends show single transition temperatures which lie between the T_g of PC and PAR. The transparency and singular transition temperatures of these blends suggest single phase blends. This, however, is not a sufficient indication that the two polymers are miscible. The observed degree of miscibility, particularly in reactive polymers, is known to be influenced by the mixing conditions and the thermal history of the blend. Are PC and PAR miscible when transesterification is minimized? To obtain additional relevant evidence a 50/50 blend was prepared by casting a film from methylene chloride solution. Also, to elucidate further the role of compounding conditions three 50/50 blends were prepared in a laboratory size, single screw extruder (3/4 inch), at low shear and at three extrusion temperatures: 285, 305, and 325 C.

The solution cast film and the extrudates at 285 and 305 C were opaque, though the latter was very slightly transparent. The extrudate at 325 C was completely transparent. The DSC plots of the extrudate at 285 C (Figure 2, bottom curve) and the solution cast film (Figure 3, bottom curve) show two transitions: the T_g of the polycarbonate phase is quite distinct, that of the polyarylate less so. Both transitions seem to have shifted slightly toward each other, indicating partial miscibility. Interestingly, the DSC curve of the cast film and the extruded blend (at 285 C) look similar. The DSC of the 305 C extrudate (Fig. 2, middle curve) also shows distinctly the T_g of the PC rich phase at around 152 C, but the transition associated with the PAR rich phase is no longer obvious. This is not to say that the blend does not have a PAR rich phase, but that the DSC is probably not sensitive enough to detect it. The DSC curve of the 325 C extrudate (Fig. 2, upper curve), which was totally

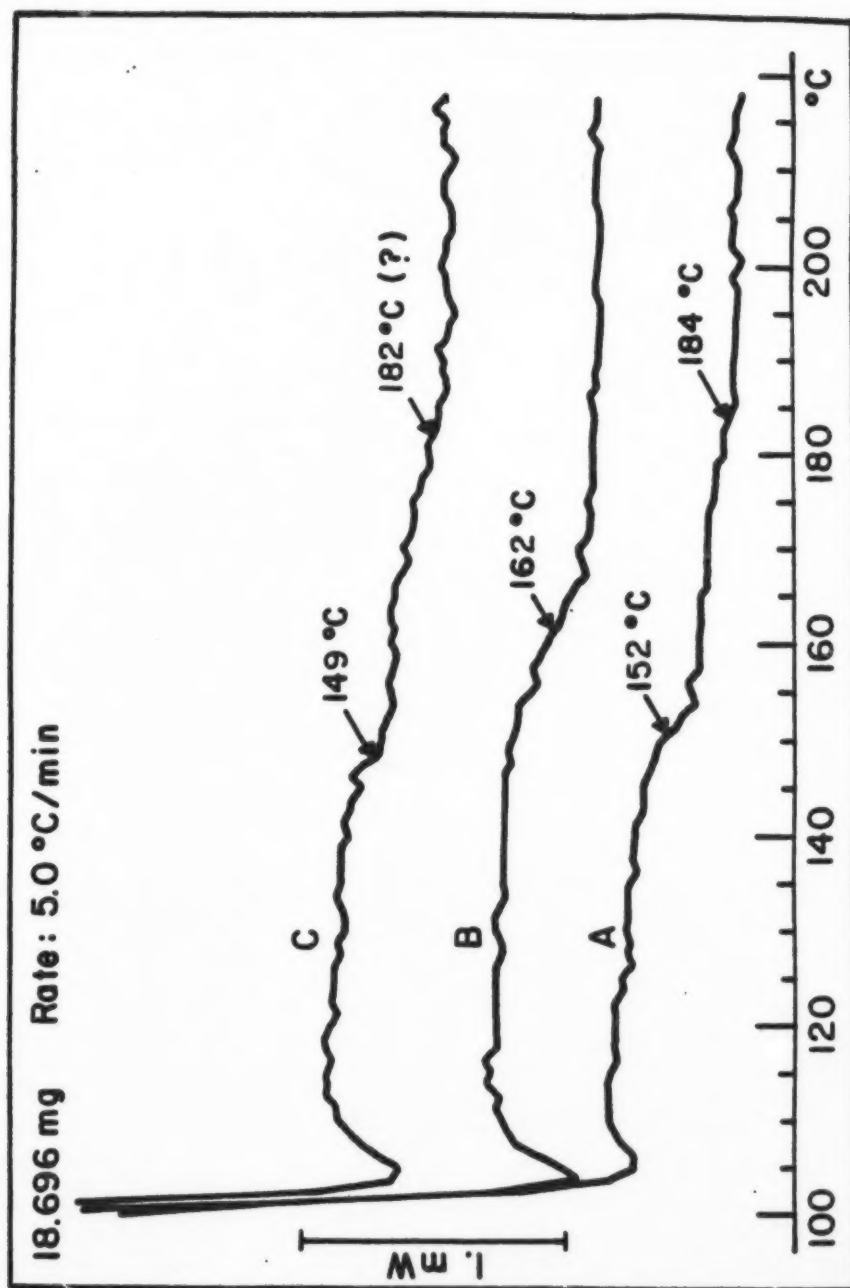


Figure 4. DSC curves of PC/PAR blends (50/50): A) reproduction of curve 1 of Fig.2, B) injection molded A, and C) sample of B dissolved in methylene chloride and cast into a film.

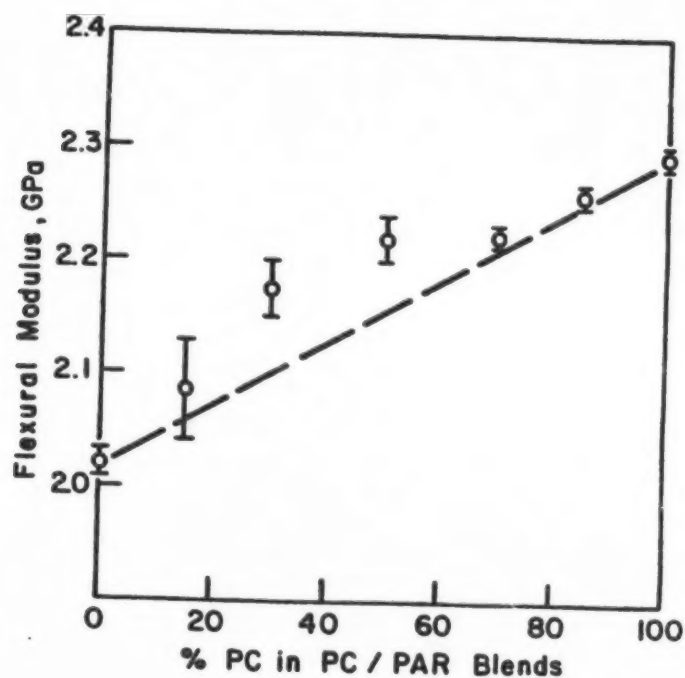


Figure 5. Flexural modulus of PC/PAR blends prepared in a twin screw extruder.

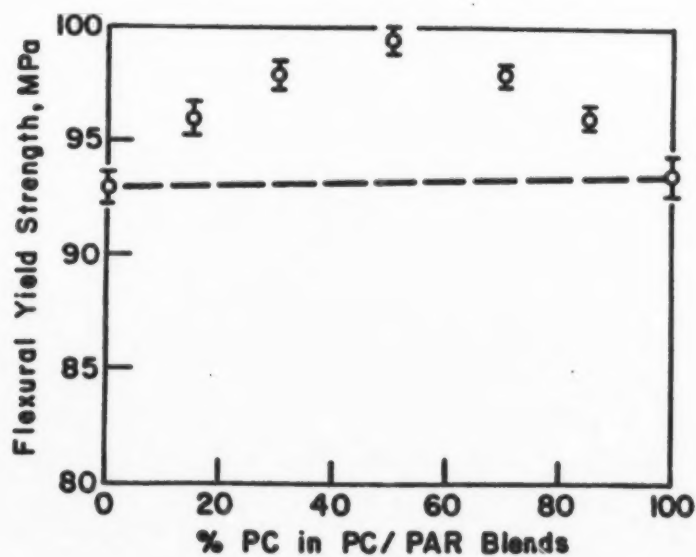


Figure 6. Flexural yield strength of PC/PAR blends prepared in twin screw extruder.

transparent, exhibits a distinct single T_g at about 160 C and, hence, is a single phase blend.

As blends are usually processed further (injection molding, blow molding, etc.) to produce useful articles, it is interesting to know how does such processing affect the phase behavior of the multi-phase PC/PAR blends. Thus, the 285 C extrudate was injection molded at melt temperature of about 290 C. The molded specimens were now transparent (a slight haze could be seen at some angles) and the DSC curve of a molded sample (Fig. 4, curve B) exhibits a single T_g at about 162 C, in contrast to the two transitions observed before molding, which is illustrated again in Fig. 4, curve A, for comparison (curve A is a reproduction of the bottom curve of Figure 2). Molded samples of the 305 and the 325 C extrudates were also transparent, but had no haze, and were darker than the 285 C specimens. But their DSC curves were very similar, all three blends showing single transition at 160 to 163 C. These observations indicate that molded articles of PC/PAR blend would, in all likelihood, be single phase.

A molded sample which corresponds to curve B in Fig. 4 and appears to be miscible, was dissolved in methylene chloride and cast into a film. The DSC trace of that film is curve C, Fig. 4. It is interesting to note the reappearance of the transition around 149 C, which corresponds to the PC rich phase. The transition associated with the PAR rich phase is not clearly visible but may still exist, as was also the case with the 305 C extrudate (Fig. 2). A solution cast film was also prepared from the 50/50 blend that was compounded in the twin-screw extruder. The DSC plot of that film is shown in Fig. 3, upper curve. It is evident that in this case the dissolution in methylene chloride did not induce phase separation. Probably, ester exchange was too advanced in this blend to result in phase separation. That an apparently miscible blend of PC/PAR can be separated is, in principle, an important observation. It suggests that the kinetics of phase separation plays an important role in the observed miscibility of blends that are prepared by melt mixing, particularly when the miscibility of the constituents is on the border line.

The data presented above suggest that PC and PAR are only partially miscible. This is also evident from the studies of Robeson⁽⁴⁾ and Kimura and Porter⁽⁷⁾. On the other hand, Mondragon et al.⁽⁶⁾ and Eguiazabal et al.⁽⁵⁾ reported a single transition at about 160 C for a 50/50 blend prepared by casting from solution. It must be said that in the latter two studies the solution cast films were kept at 300 C for 10 to 20 minutes before scanning in the DSC. Devaux et al.⁽⁸⁾, using model compounds, have studied specifically the exchange reactions of PC and PAR. Their data indicate that ester exchange reaction would be in an advanced state if the blend were exposed to 300 C for that time period. Direct evidence of the extent of the exchange reaction is difficult to have and, possibly, the formation of only some block copolymer of PC-PAR, which may act as a compatibilizer, is sufficient to bring about a single phase blend. Thus, the results of this study support the conclusion of Robeson and Kimura and Porter that blends of PC/PAR are phase separated unless conditions to yield ester exchange reaction are employed.

II. Mechanical Properties

The flexural modulus and flexural strength of injection molded specimens of the blends that were prepared by compounding in a twin-screw extruder are shown in Figures 5 and 6. The flexural strength show a positive synergistic effect with

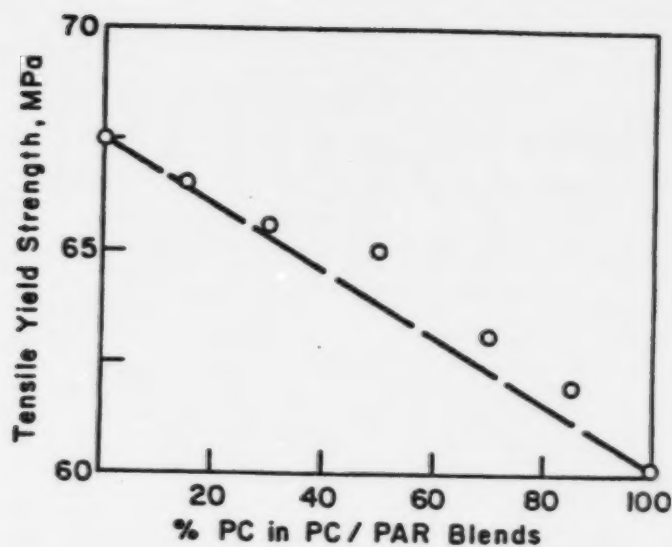


Figure 7. Tensile yield strength of PC/PAR blends prepared in a twin screw extruder.

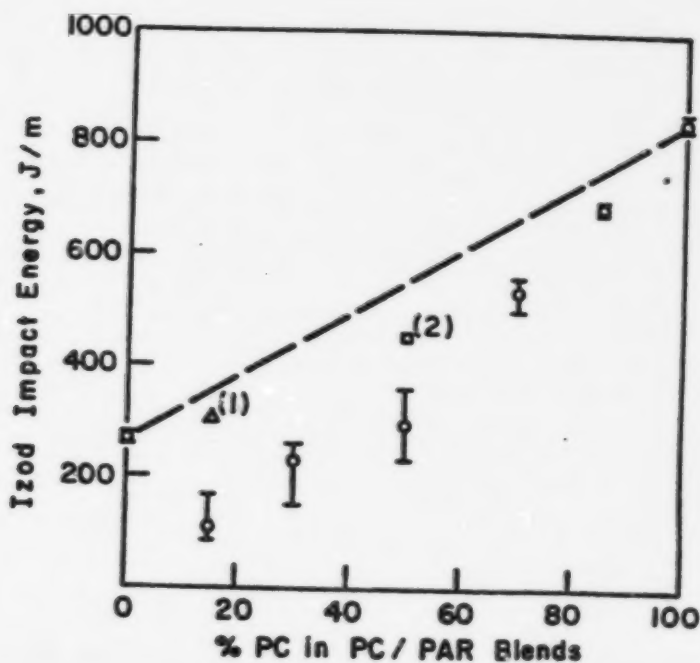


Figure 8. Room temperature Izod impact energy (1/8" thick) of:
 A. Twin screw blends (circles); B. Dry blended pellets of PC and PAR injection molded with no extrusion (point 1); C. Single screw blend extruded at 285 C (point 2).

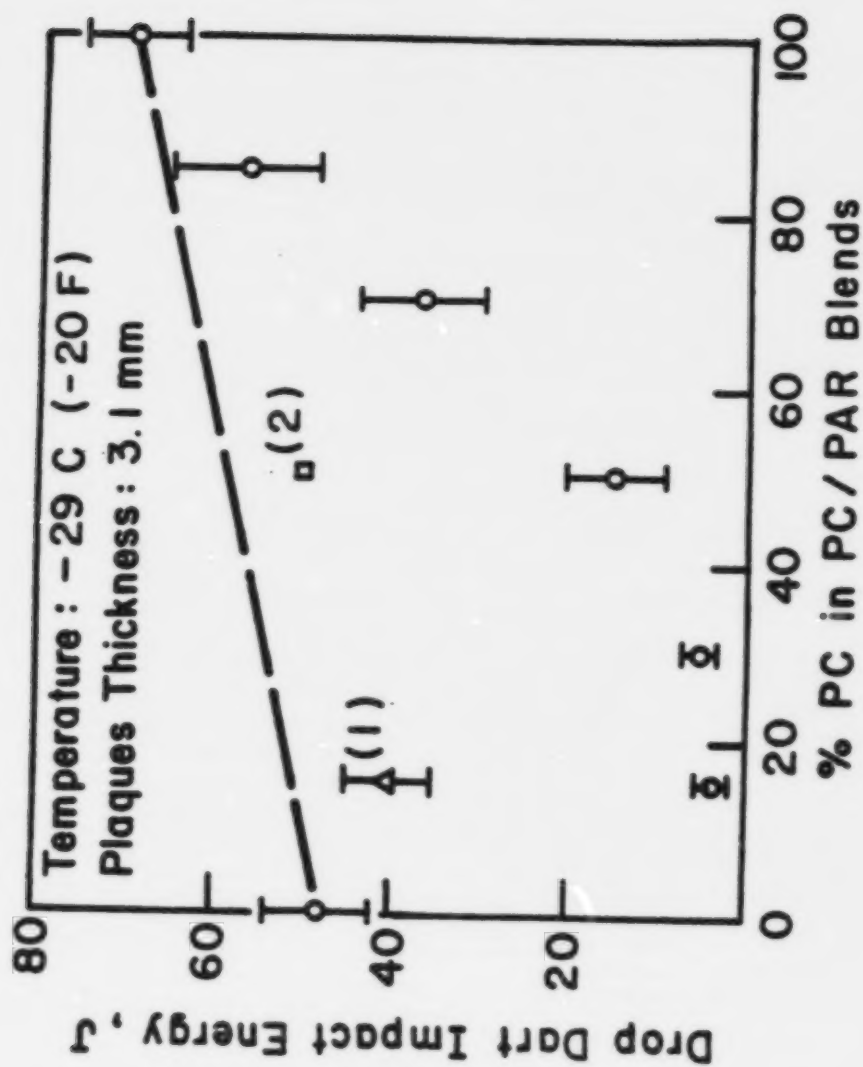


Figure 9. Dart impact energy of: twin screw blends (circles); dry blended pellets of PC and PAR molded without extrusion compounding (point 1); and single screw blend extruded at 285 C (point 2).

a maximum strength of about 99 MPa at equal weight fractions of PC and PAR. The flexural modulus also show some positive synergism but is less pronounced. The largest deviations here from the additive rule of mixtures seems to be at 30 and 50% PC. The PAR rich blends (i.e. 70 and 85% PAR) are just above the predicted values of the additive rule.

The tensile yield strength is shown in Figure 7. A small positive deviation from the additive rule of mixtures is observed in the PC rich blends. Injection molded specimens of the 50/50 blends, which were prepared in the single screw extruder at 285, 305, and 325 C, also yielded at 65 MPa. This would suggest that, in the temperature range of this study, the tensile yield strength is not very sensitive to the mixing conditions. The elongation to break, on the other hand, was found to be very sensitive to the thermal history. All the blends were ductile, having a yield point at 7 to 9% elongation and exhibiting pronounced necking before breaking and, in that regard, were similar to the parent polymers. But the elongation to break was considerably lower than would be expected from the rule of mixtures, particularly in the PAR rich blends. With the exception of the 85% PC blend, all the specimens, which were prepared in the twin screw extruder, broke below 50% elongation and, in the case of the 85% PAR blend, the elongation to break was only 15 to 20%. (The elongation to break of PC and PAR homopolymers is about 130 and 60%, respectively.) When the extrusion conditions were relatively mild then the elongation to break was in line with the rule of mixtures. For example, the 85% PC blend broke at 86% elongation and molded specimens of the 285 C blend (50/50; single screw extruder) at 87% elongation. The observed low values of the elongation to break of the blends that were prepared in the twin-screw extruder are believed to be due to the decrease in molecular weight which occurred during processing.

Of the mechanical properties investigated, the largest difference between PC and PAR is seen in impact strength. For example, the notched Izod impact energy of 1/8" thick specimens of PC is about 850 J/m (16 ft*lb/in) and that of PAR about 220 J/m. The results of notched Izod testing are plotted in Figure 8 and the dart impact data in Figure 9. The impact data of the 50/50 blend, which was prepared in a single screw extruder at 285 C, and the 85% PAR blend, which was injection molded without first compounding the PC and PAR, are also plotted for comparison and are marked (1) and (2). The notched Izod impact data of all the blends are well below the predicted values of the rule of mixtures. In the blends with 70 and 85% PAR, moreover, the impact energy falls below that of the PAR homopolymer. These results are probably a consequence of the molecular weight degradation which was more pronounced in the PAR rich blends. It is very difficult to separate the influence of composition from that of changes in molecular weight. To a first approximation, however, one may rely on the results for the blends with minimum molecular weight loss. Thus, the results for the PC rich blends, as well as the 50/50 blend which was extruded at 285 C and the 85% PAR blend that was molded without extrusion, fall between the Izod impact values of the parent polymers. Since these blends exhibited very little molecular weight degradation, it may be assumed that their impact results reflect the influence of blend composition and that the observed negative synergism is real.

The results of direct impact of plaques at -29 C (-20 F) are shown in Figure 9. It is clear that blending resulted in reduction of impact energy. The 15% PAR blend and the 50/50 blend (single screw, 285 C) are comparable in impact energy to PAR. The other blends, however, exhibit a substantial loss in impact

energy, a large part of it probably due to degradation. The 85% PAR blend that was molded directly also has an impact energy below that of PAR. While in this case molecular weight degradation during molding was negligible, it is possible that the low impact energy is due to poor mixing. Thus it appears from the results presented above that the impact properties of PC/PAR blends show negative deviation from the additive rule of mixtures which is further compounded because of degradation in molecular weight and, possibly, ester exchange reactions.

CONCLUSIONS

When carefully prepared, blends of PC and PAR are only partially miscible: two transition temperatures, corresponding to a PC rich phase and to a PAR rich phase are clearly seen in solution cast blends and in blends that are extruded at 285 C. Ester exchange reaction of PC and PAR results in a miscible system, probably, due to the formation of a copolymer which acts as an effective compatibilizer. It appears that very little reaction causes miscibility and, hence, in practical situations, which usually involve compounding and subsequent molding, the PC/PAR blends would invariably exhibit single phase behavior.

The tensile and flexural properties of the blends show some positive synergism and the impact properties a pronounced negative synergism. On balance, the blending of PC and PAR, without containing the exchange reactions, does not appear to result in a material with improved mechanical performance.

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